Petroleum Refinery Life Cycle Inventory Model (PRELIM)

PRELIM v1.5

User guide and technical documentation

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PRELIM and PRELIM Documentation Change Record

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Terminology: Acronyms and Abbreviations

Table Acronyms and abbreviations

Acronyms and Abbreviations	Description
%wt	Percentage on weight basis e.g., 1gram per kilogram equals 0.1 %wt
+°C	Temperature over specific value in Celsius
AGO	Atmospheric gas oil
AR	Atmospheric residue
CCQMP	Canadian crude quality monitoring program
CHP	Cogeneration of heat and power
CVRSMD	Coefficient of variation of the root-mean-square deviation
FCC	Fluid catalytic cracker
GHG	Greenhouse gas
GO-HC	Gas oil hydrocracker
H	Hydrogen
HHV	High-heating value
HTSD	High temperature simulated distillation
HVGO	Heavy vacuum gas oil
iC5	Isopentane
KW	Watson characterization factor
LCA	Life cycle assessment
LHV	Low-heating value
LPG	Liquefied petroleum gas
LSR	Light straight run
LVGO	Light vacuum gas oil
MCF	Million cubic feet
MCR	Micro carbon residue
NG	Natural gas
NCR	Naphtha catalytic reforming/reformer
PADD	United States Petroleum Administration for Defense District
PFD	Process flow diagram
PRELIM	Petroleum refinery life cycle inventory model v1.3, unless otherwise stated.
RFG	Refinery fuel gas
S	Sulphur
SARA	Saturate, Aromatic, Resin, and Asphaltenic
SD	Standard deviation
SMR	Steam methane reforming
SR	Straight run
t	Metric tonne
TBP	Temperature boiling point
ULSD	Ultra-low sulphur diesel
Vol	Volume
VR	Vacuum residue

Part I Introduction and User Guide

1   Working with PRELIM: a quick reference guide

This section provides a summary of the documentation to give the user a quick overview of PRELIM's main features.

1.1   Technical requirements

PRELIM is a stand-alone, spreadsheet-based model that operates in Microsoft Excel. It has been successfully tested with Microsoft Excel 2007, 2010, 2013, and 2016 for PC and Macintosh.

PRELIM is a complex Excel spreadsheet that can be resource-intensive for some computers and can result in stability issues in Excel. If this happens, restarting the computer prior to launching the PRELIM model may resolve the issue.

1.2   Running a crude oil assay from the assay library

The `Main Input & Output` worksheet contains all the main options to run the model for one or all crude assays available in the model including a custom assay.

The user can run a crude assay in PRELIM by selecting the assay in the dropdown menu of the `Basic input` section. The properties of the active assay are available below in the PRELIM format (see section 2.3.2.4 to learn about the format). The main results in terms of energy use, and environmental impacts assigned to the impact categories included in the US EPA Tool for the Reduction and Assessment of Chemical and Environmental Impacts (TRACI) life cycle impact assessment (LCIA) method are displayed in real time to the right of the input cells in the `Main results` box.

Detailed results are available on the `Results Single Assay` worksheet. Additional details for the two main types of refinery are displayed on the `CokingRefinery Detailed Results` and the `HydroRefinery Detailed Results` worksheets.

The user can also run the model for all crude assays available in the assay inventory by clicking the `All assays in inventory` button available in the `Additional inputs and options` section.

A set of dropdown menus and checkboxes listed in the `Additional inputs and options` section of the `Main Input & Output` worksheet allow the user to override some default settings, including options for Naphtha Catalytic Reformer (NCR) and Fluid Catalytic Cracker (FCC) hydrotreater, the source of electricity consumed, the allocation method and the allocated products for GHG emissions and energy use, the heating value calculation basis, global warming potential values, and the inclusion of waste management GHG emissions, asphalt production, LPG and petrochemical production, refinery fuel gas (RFG) production, and cogeneration.

Newly added options in PRELIM 1.5 on the `Main Input & Output` worksheet include: 1) on/off switches for naphtha hydrotreater (NHT), kerosene hydrotreater (KHT), and diesel hydrotreater (DHT). Users can choose whether these hydrotreaters are in use. These functions also have updated hydrotreated jet/kerosene and diesel densities. 2) a region selection function has been added in which users can choose where refining takes place. Unit yield patterns, intermediate flow split ratios (to downstream units), and utility rates that are associated with jet production are updated for each region using regional average values. 3) a second LHV and HHV prediction method based on American Petroleum Institute-Technical Data Book- Petroleum Refining. 4) direct separation of Naphtha, Atmospheric Residual (AR), Light Vacuum Gas Oil (LVGO), and Heavy Vacuum Gas Oil (HVGO) as products

for sale. Their production can be access via the `CokingRefineryCalcs` worksheet Cells K132, P45, K549, and L549 and the `HydroRefineryCalcs` worksheet Cells M119, Q45, K523, and L523, respectively. Users can choose if emissions are allocated to them. 4) energy use of all main process units (including heat, gas, and steam requirements) is updated by using regional average values.

1.3 Advanced options

The `Expert Input` worksheet provides users with additional tools (details in Section 3.2), such as running a custom crude assay, blending multiple crude assays, and optimizing the product slate.

2   Introduction

The Petroleum Refinery Life Cycle Inventory Model (PRELIM) is a mass- and energy-based, process unit-level tool for estimating the energy use and GHG emissions associated with processing a variety of crude oils within a range of configurations in a refinery. The latest version of the model as of April 2019 (v1.3) now includes Life Cycle Impact Assessment (LCIA) to estimate a variety of environmental impacts based on characterization factors provided by the Tool for the Reduction and Assessment of Chemical and Environmental Impacts (TRACI, US EPA). PRELIM aims to inform decision making and policy analysis by providing a transparent model including data, assumptions and detailed results.

This user guide and technical documentation introduces PRELIM and presents modelling methods, calculations, and data sources. First, this introduction section describes PRELIM's motivation and overall goals. It also outlines the general components of the model with a brief description of the software and modelling systems used. Then, an interface guide introduces the PRELIM interface and outlines how users can interact with each of the interface worksheets. Next, the technical documentation section details the modelling methods, modelling structure, default specifications, and assumptions used within the calculation worksheets to estimate the energy use and associated GHG emissions for each process unit and at a global refinery level. Finally, the model evaluation section describes the methods used to validate PRELIM calculations as well as modelling methods. It also includes implications of PRELIM enhancements in model results. Details of the changes made to the model with the release of each new version is documented in Appendix A.

The PRELIM model was built using Microsoft Excel to ensure transparency and maximum accessibility. PRELIM is freely available for download from the Life Cycle Assessment of Oil Sands Technologies research group website (University of Calgary): http://ucalgary.ca/lcaost/prelim.

2.1   Model motivation

PRELIM was developed to offer a free, flexible, transparent, and open-source tool that captures the impact of crude oil quality and refinery configuration on energy use and environmental impacts associated with refining crude oils. It combines a life cycle approach with linear programming modeling methods to overcome existing life cycle model limitations. Further documentation and examples can be found in Abella et al. (2012).

The potential use of PRELIM includes running scenarios for policy analysis purposes to explore the implications of processing crudes of different qualities and in different refinery configurations as an example. The target audience includes researchers and decision-makers from government, academia, and industry.

2.2   PRELIM model goals

The release of the PRELIM model as an open source tool had the following objectives:

1. Build a rigorous, engineering-based model to estimate energy use and GHG emissions from crude oil processing in a refinery, using a life cycle approach;
2. Work with refinery experts to validate assumptions and data;
3. Use detailed data (public wherever possible) to provide maximum accuracy and flexibility;
4. Document sources of all equations, parameters, and input assumptions;
5. Provide a model that is free to access, use, and modify by any interested party; and
6. Provide a data framework that can be integrated as a module in a Well-To-Wheels (i.e., life cycle) model.

Comprehensive documentation is intended to allow effective use and modification of the tool by the user. This document explains PRELIM's calculations and assumptions and provides information on model data sources. Users can find additional documentation about data input and features that can be overridden in each worksheet of the model.

2.3 PRELIM model construction

2.3.1 Software system

PRELIM is a stand-alone, spreadsheet-based model that operates in Microsoft Excel. It has successfully been tested with Microsoft Excel 2007, 2010, 2013, and 2016 for PC and Macintosh.

PRELIM is a complex Excel spreadsheet that can be resource-intensive for some computers and can result in stability issues in Excel. If this happens, restarting the computer prior to launching the PRELIM model typically resolves the issue.

2.3.1.1 Organization

PRELIM is divided into four types of worksheets: (i) Summary worksheets (**sheet tab color: black**), (ii) inputs and results worksheets (**sheet tab color: red**), (iii) calculation worksheets (**sheet tab color: blue**), and (iv) data and constants worksheets (**sheet tab color: green**):

- The summary worksheets include an `Overview` worksheet that provides an author list, past and current versions of the model, a brief description of each worksheet, a copyright statement, and a `ChangeLog` worksheet that summarizes changes and updates.
- The inputs and results worksheets include a user interface and provide all basic options to run the model and display live updates to the main results. The calculation worksheets are where most, if not all, of the calculations take place using specific modelling methods at both process unit and system level.
- The data and constant worksheets support the calculation worksheets with fundamental data (i.e., PRELIM default technical specifications database that can be overridden by advance users) and supporting data (i.e., necessary data for inputs to outputs data transformation).

Figure 1 shows an overview of PRELIM software system organization.

PRELIM

Summary	Inputs and Results worksheets	Calculations Sheets	Data and Constants Worksheets	OpenLCA
• Overview	**Objective: User Interface**	**Objective: Detailed Modelling**	**Objective: Default Specifications**	**Objective: Allow export to OpenLCA**
• Changelog	• Main Input & Output	• Modelling Methods	• Constants	• General Information
	• Main Input Box	• Configuration and Process Energy Requirements	• Energy & Unit Conversions	• Inputs
	• Main Results Box	• Hydrogen addition processes and global hydrogen mass balance method	• Process Correlations	• Outputs
	• 1st Resultsdetail	• Carbon rejection processes and product yields	• Emission Factors	• Allocation
	• Expert Inputs	• Alternative value added processes	• TRACI CFs	
	• Input Custom Assay Selection	• Environmental impact calculations	• Assay Inventory	
	• Input Crude Blender Box	• PRELIM crude assay inventory (External Calculations)		
	• Product Slate Optimization Procedures			
	• Jet-Diesel Swing	• Modelling Structure		
	• Octane and Cetane Procedures	• Process Flow Diagrams		
		• HydroRefineryPFD		
		• CokingRefineryPFD		
		• Calculations		
		• CokingRefineryCalcs		
		• HydroRefineryCalcs		
		• Controls		
		• CokingRefineryControls		
		• HydroRefineryControls		

Figure 1: Overview of PRELIM software system organization

2.3.1.2   Color-coding

PRELIM model uses a color-coding system to help users navigate the model: the summary worksheet tabs are black, the inputs and results worksheet tabs are red, calculations worksheet tabs are blue, and data and constant worksheet tabs are green.

In addition, the following color-coding is used in the spreadsheets:

- **A cell with a red background** indicates that this value is a constant and can be overridden by expert users either in the `Constants` worksheet or directly in the cell;
- **A value with a white background** typically indicates a calculated value; and
- the `Process Correlations` worksheet uses a specific color-coding for results, inputs, and assumptions data that is indicated at the top of the spreadsheet.

Some color-shading is also used in this document to help navigate the documentation:

- `This format` refers to a worksheet in the PRELIM model; and
- `This format` refers to a header or an option in the PRELIM model.

2.3.2   Modelling system

2.3.2.1   Approach

PRELIM employs a systems level approach and refinery linear modelling methods. A range of configurations are constructed to reflect current operating refineries in North America. The systems level approach ensures wide applicability in assessing energy use and environmental impacts for processing crudes of different quality and allows for incorporation of model results into Well-To-Wheel analyses. Refinery linear modelling methods are adopted for both individual process units and overall refinery mass balance. This modelling approach facilitates exploration of the use of different life cycle inventory allocation methods at the refinery sub-process level. As the model structure allows for the integration of key life cycle assessment concepts (i.e., goal and scope definition, system boundary, functional unit, and allocation) as recommended by the International Standard ISO 14041, the model itself is therefore titled the Petroleum Refinery Life-cycle Inventory Model (PRELIM).

The two main inputs required to run PRELIM are refinery configuration and crude quality information (described in sections 2.3.2.3 and 2.3.2.4).

2.3.2.2   Boundaries

The system boundary of PRELIM includes all major process units used in a refinery to process petroleum crude oil. Up to twenty-four process units can be enabled within one of eleven available configurations. The system boundary also includes the upstream energy use and environmental impacts associated with input energy sources (i.e., electricity and natural gas).

Upstream (e.g., extraction, processing, transport) and downstream (e.g., transport, use of transportation fuel in a vehicle) energy and environmental impacts are not included in PRELIM.

PRELIM focuses on combustion emissions. Fugitive GHG emissions are not considered in the current version.

2.3.2.3   Structure – PRELIM refinery configurations

PRELIM simulates eleven refinery configurations. All configurations (except for the Asphalt Configuration) include crude distillation, hydrotreating, naphtha catalytic reforming (NCR), isomerization, steam methane reforming, and pollution control such as flue gas treatment and sulphur recovery. Additional process units, based on refinery configuration selection, can be enabled including gas oil hydrocracking, fluid catalytic cracking, coking, and residual hydrocracking.

Figure 4 and Figure 6 in section 5.2 display process flow diagrams (PFD) for each of the major refinery configurations (note that supporting process units are not displayed on the PFDs).

Calculations for all configurations are structured within the arrangement of and relations between the process units of two major refinery types: coking refinery and hydrocracking refinery (also called hydro refinery). The set of calculations in both types include calculations for the basic processes described above plus gas oil hydrocracking and/or fluid catalytic cracking. They differentiate themselves by the specific calculations to model either the delayed coking or the residual hydrocracking process units; both are mutually exclusive deep conversion processes that interact in different ways with other process units and yield different products.

The first four refinery configurations (0 as hydroskimming; 1, 2, and 3 as medium conversion), generate identical calculations sets and results for both refinery types: coking refinery and hydrocracking refinery (see section 5.2 for more details). Configurations 4, 5, and 6 (deep conversion) are specific to the coking refinery calculations set, and configurations 7, 8, and 9 (deep conversion) are specific to the hydro refinery calculations set.

The calculation structure allows PRELIM to run and display results simultaneously for both coking and hydrocracking refinery with the caveat that the user can select configurations 4 to 6 only within the coking refinery modelling structure and configurations 7 to 9 only within the hydrocracking modelling structure. Results are shown real time in the main and detailed results worksheets in terms of energy use and GHG emissions.

2.3.2.4   Database - PRELIM crude assay inventory

PRELIM uses crude oil quality information as the starting point for model calculations. This information is typically available in the public domain as a crude oil "assay". However, the format of this information is presented in a variety of formats. As such, it might not be presented in a format that can be readily incorporated into PRELIM. In

such cases, the assay must be converted to PRELIM specific format. The PRELIM format uses five parameters to characterize the quality of a crude oil: crude distillation curve, sulphur content, API gravity, carbon residue content, and hydrogen content. The crude is also divided into nine fractions, each associated with a specific cut-temperature. The five quality parameters are also specified for each of the nine fractions in addition to the whole crude. A total of 62 parameters are required by PRELIM for each run. Figure 2 provides an example of a crude oil assay in PRELIM format.

Belridge_Knovel		BRG					Crude specific destillation curve				
Assay #	26	Cutoff Temp [°C]	80	175	295	340	400	455	530	530.00 +	397.00 +
Property	Units	Full Crude	LSR	Naphtha	Kerosene	Diesel	AGO	LVGO	HVGO	VR	AR
Vol Flow	bpd	99,407.1	1,257.6	2,291.1	8,746.2	5,346.0	11,547.1	2,073.0	7,130.8	61,015.3	69,205.9
Vol Flow	m^3/d	15,805.7	200.0	364.3	1,390.6	850.0	1,836.0	329.6	1,133.8	9,701.4	11,003.7
Mass Flow	kg/d	15,359,400.0	153,594.0	307,188.0	1,228,752.0	767,970.0	1,689,534.0	307,188.0	1,075,158.0	9,830,016.0	11,212,362.0
Sulphur	wt%	0.2	0.0	0.0	0.0	0.1	0.2	0.4	0.6	0.1	0.3
Nitrogen	mass ppm	8,382.9	0.0	0.0	50.0	1,000.0	1,390.2	2,203.4	3,116.3	8,000.0	11,200.0
API gravity	oAPI	15.0	52.5	36.1	28.5	25.0	22.1	20.2	17.6	8.0	7.2
Density	kg/m^3	966.0	768.1	843.3	883.6	903.5	920.2	932.0	948.3	1,013.3	1,019.0
Hydrogen	wt%	10.6	11.7	11.9	11.8	12.2	11.9	11.8	11.5	9.9	10.1
MCR	wt%	5.9								9.2	8.1
Characterization Factor	Kw (Approximate)	12.0	10.7	10.9	11.1	11.2	11.4	11.6	11.8	11.9	11.9
Tb(50%) weight basis	[°C]	600.0	40.0	160.0	250.0	310.0	375.0	430.0	510.0	700.0	710.0

Figure 2: An example of crude oil assay in PRELIM format

PRELIM includes a crude assay inventory with oil assays in the PRELIM format. As of April 2019, there are 144 crude oil assays in this inventory. However, crude oils are being added to the inventory regularly. Some examples of the cut temperatures used in original Chevron, Exxon, BP and Statoil assays are presented in Table 1. Permission was granted from these sources to use these data. PRELIM also allows a user to input a custom assay as well as to blend multiple assays into a blended assay.

Table 1: Cut temperatures in Chevron, Exxon, BP and Statoil Assays

	C5s	Naphtha	Kerosene	Diesel	AGO	LVGO	HVGO	VR	AR				
Cutoff Temp (End) in Model [°C]	80	180	290	343	399	454	525	525	399				
BP[1]	C5-95	Naphtha	Naphtha	Kerosene	Atm Gas Oil	Vac. Gas Oil	Vac. Gas Oil	Heavy Vac. Gas Oil	Residue				
	95	149	175	232	342	369	509	550	585				
Chevron[2]	Light Naphtha	Medium Naphtha	Heavy Naphtha	Kerosene	Atm Gas Oil	Light VGO	Heavy VGO	Vacuum Residue	Atm Residue				
	80	150	200	260	340	450	570	End	End				
Exxon[3]	Butane and Lighter	Light Naphtha C5	Heavy Naphtha	Kerosene	Diesel	Vacuum Gas Oil	Vacuum Residue						
	15	74	165	250	343	537	815						
Stat Oil[4]	Atmospheric Cuts									Vacuum Cuts			
	65	100	150	200	250	300	350	370	FBP	450	500	550	FBP

[1] Source: http://www.bp.com/en/global/bp-crudes/assays.html (last accessed on September 1st, 2014)
[2] Source: http://crudemarketing.chevron.com (last accessed on September 1st, 2014)
[3] Source: http://www.exxonmobil.com/crudeoil (last accessed on September 1st, 2014)
[4] Source:
http://www.statoil.com/en/OurOperations/TradingProducts/CrudeOil/Crudeoilassays/Pages/default.aspx (last accessed on September 1st, 2014)

> Knovel assay format is not mentioned in this table because Knovel assay format can slightly vary from one assay to another. You can learn more about the Knovel assay formats at this URL: http://app.knovel.com

The method used to convert an original crude oil assay into PRELIM format is explained in section 5.5.1 as well as in Abella et al. (2012). This method has been evaluated as described in section 0.

3 A guide to the user interface

The `Input and Output` worksheets (**sheet tab color: red**) work as the main user interface that allows the selection of both basic and advanced options and presents users aggregated and detailed modeling results. They can be used to run one or all crude oil assays included in the assay inventory.

These worksheets do not contain any calculations since their purpose is to select/provide inputs to the model and display results. The section below presents the interface, how the user can interact with the model as well as the links between the worksheets.

3.1 Main Input & Output

The `Main Input & Output` worksheet has two main functions:

1. Provide all basic options to run the model for one or all crude oil assays; options are on the left side of the worksheet and grouped in the `Main inputs` box.
2. Display live updates to the main results for the selected assay; main results are on the right side of the worksheet and grouped in the `Main results` box

> Note: All input parameters are prepopulated with default values and options, and any change will trigger the model to recalculate the results.

3.1.1 Main inputs box

The main user interactive inputs include:

- **Buttons that contain hyperlinks** to allow the user to access other worksheets of the model relevant to an activity;
- **Buttons that activate macros** to run specific features of PRELIM such as running all assays in the assay inventory; and
- **Dropdown menus and checkboxes** that are built using Excel form controls. These form controls are not linked to macros but are linked to cells located on the calculation worksheets (**sheet tab color: blue**).

Each time the file is opened, PRELIM loads the dropdown menus and checkboxes with the same choices that were active when the model was last saved. When a new crude assay is selected, the model automatically updates the active refinery configuration for both of the two major refinery modelling structures/calculation sets using the methods described in section 5. However, there is one exception to this: the active configuration is *not* updated if the user has overridden it by forcing the use of a specific configuration in the `Process unit configuration` option in the `Main input & Output` worksheet. Selecting `Default value` in the dropdown menu will allow PRELIM to use again the default calculated value.

3.1.1.1 Basic input

The first section in the `Main Input & Output` worksheet, under the header `Basic input`, provides a crude oil assay dropdown menu. When the user selects a new assay from the inventory, the selected crude assay's properties are copied from the `Assay Inventory` worksheet and displayed in the table below the dropdown menu in PRELIM format. Note that selecting another crude oil assay automatically triggers the model to recalculate and overwrite the energy and GHG emissions using the new crude assay data. The `Main results` box to the right of the inputs is also automatically updated.

3.1.1.2   Other inputs and options

The second section, `Additional inputs and options`, offers users additional options. This section includes three subsections highlighted with a dark blue background:

1. `More options`
2. `Display detailed results`
3. `Additional inputs and options`

3.1.1.2.1   More options

The `More options` subsection includes five buttons:

- `View assay inventory` links to the `Assay Inventory` worksheet tab and displays all the crude oil assays available in the model in PRELIM format. Any changes to an assay can only be made in the `Assay Inventory` worksheet tab;
- `Input custom assay` links to a blank section in the `Expert Input` worksheet tab where users can add a custom crude oil assay in PRELIM format. Once added to the table, the user must select `Use Custom Assay` in the `Basic input` dropdown menu to run the new assay; and
- `Create crude blend` links to the `Crude blender` tool in the `Expert Input` worksheet that allows users to blend up to 10 (ten) crude assays from the assay inventory by mass ratios. Once completed, the user must select `Use Custom Blend` in the `Basic input` dropdown menu to run the created blend in the model (see 3.2.2 for more details).
- `Hydrotreater hydrogen sensitivity` allows users to specify the minimum and maximum outflow hydrogen content of each hydrotreater to quantify how the energy and emissions estimates change due to changes in these assumptions.

3.1.1.2.2   Display detailed results

The `Display detailed results` subsection has two buttons allowing further exploration of the results:

- `Current assay` displays a second level of detailed results for the current assay available on `Results Single Assay` worksheet. These results are more detailed than the `Main results` box on the `Main Input & Output` worksheet.

> A third level of detailed results is available for each of the two major refinery modelling structures/calculation sets: `CokingRefinery Detailed Results` and `HydroRefinery Detailed Results` display the breakdown of energy inputs and outputs as well as the GHG emissions per process unit.

- `All assays in inventory` runs a macro (`Float all assays`) that successively runs the model for each of the crude oil assays available in the `Assay Inventory` worksheet, including the `Custom Assay` and the `Custom Blend` that are set in the `Expert Input` worksheet.

> Note: Running the `All assays in inventory` macro can take up to 2 minutes on some computers. These include Macintosh computers due the fact Microsoft Excel software differs quite significantly from PC's version. It is recommended that users avoid doing anything else on the computer while the macro is running. The macro will automatically redirect the user to the `Results All Assays` worksheet once the process is completed.

3.1.1.2.3 Even more inputs and options

The `Even more inputs and options` subsection allows users to define additional inputs and options such as refinery configuration, allocation method, products that emissions should be allocated to, and heating values used in model calculations (i.e., High heating value - HHV vs. Low heating value- LHV).

3.1.1.2.3.1 Refinery configuration

This set of options allows the user to enable or disable processes in the coking refinery and hydrocracking refinery modelling structures/calculation sets. These options include:

- `Process unit configuration`: each crude oil assay is associated with a default configuration for both refinery modelling structures/calculation sets (see section 5.2 for details on how the default configuration is obtained). Each refinery modelling structure/calculation set has a dropdown menu that allows for selecting the `Default value` (first option) or forcing the use of a specific refinery configuration. Processes included in each of the configurations are listed in the table to the right of the override options.
- Table 2 details the process units that are enabled in each of the configurations. Sections 5.2 and 5.26 present flow diagrams of all configurations and how the process units are connected.
- `Naphtha catalytic reformer options`: this dropdown menu allows users to choose the configuration of the naphtha catalytic reformer. By default, it assumes that the unit receives straight run naphtha (`SR Naphtha`) as input. A second option in the dropdown menu assumes the SR Naphtha is combined with the stream coming from the coking/hydrocracking naphtha hydrotreater (`Heavy Naphtha`) as input to the naphtha catalytic reformer.

  Note: this option only applies if a deep conversion configuration is active.

- `FCC hydrotreater options`: this dropdown menu allows users to override the fluid catalytic cracking hydrotreating option, which by default uses a post-hydrotreater (FCCPHT) after the FCC to treat FCC gasoline. Another option in the dropdown menu allows users to choose a pre-hydrotreater (FCCFHT) prior to FCC.

  Note: this option only applies if a medium or deep conversion configuration is active. FCCFHT (83 out of 363 refineries worldwide) is not as widely deployed as FCCPHT (216 out of 363 refineries worldwide) because it may not be economically worthwhile to treat all incoming FCC feed, unless more high-quality gasoline is desired from FCC than diesel.

- `Electricity source`: this dropdown menu allows users to choose the electricity source to be used and it currently offers three options: electricity generated from a coal-fired power plant (`Coal-Fired Power Plant 100%`); electricity generated from a natural gas-fired power plant (`NG-fired Power Plant`); or electricity generated from a Low Carbon Power plant (`Low Carbon Power Plant`).

  Note: The option allows PRELIM to run and display results simultaneously for two refinery configurations with the caveat that the user can select configurations 4 to 6 only within the coking refinery modelling structure and configurations 7 to 9 only within the hydrocracking modelling structure. Simultaneous results are made available for the real time main and detailed results in terms of energy use and GHG emissions for a crude assay in two configurations and for the entire assay inventory runs.

Table 2: Process units enabled in each configuration

		Coking and hydrocracking refineries			Coking refinery				Hydrocracking refinery			Asphalt refinery
	Process units	Config. 0	Config. 1	Config. 2	Config. 3	Config. 4	Config. 5	Config. 6	Config. 7	Config. 8	Config. 9	Config. 10
Hydroskimming process units	Desalter	x	x	x	x	x	x	x	x	x	x	x
	Atmospheric tower furnace	x	x	x	x	x	x	x	x	x	x	x
	Atmospheric tower	x	x	x	x	x	x	x	x	x	x	x
	Naphtha hydrotreater	x	x	x	x	x	x	x	x	x	x	
	Isomerisation unit	x	x	x	x	x	x	x	x	x	x	
	Naphtha catalytic reformer	x	x	x	x	x	x	x	x	x	x	
	Kerosene hydrotreater	x	x	x	x	x	x	x	x	x	x	
	Merox unit	x	x	x	x	x	x	x	x	x	x	
	Diesel hydrotreater	x	x	x	x	x	x	x	x	x	x	
Medium conversion process units	Vacuum tower furnace		x	x	x	x	x	x	x	x	x	x
	Vacuum tower		x	x	x	x	x	x	x	x	x	x
	Gas oil hydrocracker		x		x		x	x		x	x	
	Gas oil hydrocracker fractionator		x		x		x	x		x	x	
	Fluid catalytic cracker feed hydrotreater		x		x	x		x	x		x	
	Fluid catalytic cracker		x		x	x		x	x		x	
	Fluid catalytic cracker main fractionator		x		x	x		x	x		x	
	Alkylation unit		x		x	x		x	x		x	
Coking units	Coking furnace					x	x	x				
	Coking					x	x	x				
	Coking fractionator					x	x	x				
	Coking naphtha hydrotreater					x	x	x				
Hydrocracking process	Residue hydrocracker furnace								x	x	x	
	Residue hydrocracker								x	x	x	
	Residue hydrocracker fractionator								x	x	x	

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Residue hydrocracker naphtha hydrotreater								x	x	x	

A high-level process flow diagram shows how all process units are connected in section 5.2. A process flow diagram for each refinery configuration is also available in section 6.

- `SMR hydrogen purification options`: this dropdown menu allows users to choose the type of hydrogen purification technology for SMR calculations. By default, PRELIM assumes that amine CO_2 removal is used for hydrogen purification. Another option in this dropdown menu refers to Pressure Swing Adsorption (PSA).
- `Naphtha, Kerosene, and Diesel Hydrotreater options`: these dropdown menus allow users to choose if they want the corresponding hydrotreaters to be included in modeling. By default, all three are set as enabled. If they are disabled, the inputs to these hydrotreaters will be the same as the outputs without any energy/hydrogen use.

3.1.1.2.3.2   Allocation Method

PRELIM presents results using two different functional units – per bbl of input crude and per MJ of final product (e.g., gasoline). This means that energy and GHG emissions can be estimated for the entire refinery or for an individual final product. To present the results per final product, allocation of energy and emissions is required. The `Allocation method` option allows users to select one of four allocation methods to process crude oil assays. Allocation is made on a process unit level and results in cumulative energy and emissions estimates for each refinery final product. Details of the four allocation methods are:

- `Mass Basis`: energy and GHG emissions are apportioned to each product exiting each unit based on the relative mass of that product as compared to the total mass exiting that unit;
- `Energy Basis`: energy and GHG emissions are apportioned to each product exiting each unit based on the relative energy content of that product as compared to the total energy content exiting that unit;
- `Market Value Basis`: energy and GHG emissions are apportioned to each product exiting each unit based on the relative market value of that product as compared to the total market value of all products exiting that unit; (see note below); and
- `Hydrogen Content Basis`: energy and GHG emissions are apportioned to each product exiting each unit based on the relative hydrogen content of that product as compared to the hydrogen content of all products exiting that unit.

> Note regarding the `Market Value Basis`: prices used to calculate the value are located at the bottom of the `Constants` worksheet. Product prices were obtained from historical North American data from Platts (http://www.platts.com/product-list/all/all/market-data) and CMAI (www.cmaiglobal.com). These numbers can be overridden.

3.1.1.2.3.3   Allocation to products

PRELIM by default focuses on exploring the impacts of refining transportation fuels, including `Blended Gasoline`, `Jet-A/AVTUR`, and `ULSD` (Ultra Low-Sulphur Diesel) that are considered in all configurations. The `Allocation to products` option allows users to assign energy use and emissions to more final products. Nine

products are optional and can be enabled or disabled depending on refinery configuration and if they are produced: `Fuel Oil`, `Liquid Heavy Ends`, `Surplus NCR Hydrogen`, `Coke/HC residue`, `Sulphur`, `RFG`, `LPG`, `Petrochemical Feedstocks`, and `Asphalt`. Starting from PRELIM 1.5, three more products including `Atmospheric Residue`, `Naphtha`, and `VGO` are included via direct separation.

3.1.1.2.3.4   Heating value

This dropdown menu offers a choice in the heating value used in the model: `Lower Heating Values (LHV)` or `Higher Heating Values (HHV)`. The heating value of a product corresponds to the amount of heat released during the combustion of that product. Starting from PRELIM 1.5, a second LHV/HHV prediction method based on American Petroleum Institute-Technical Data Book- Petroleum Refining is added (See Energy & Unit Conversions Tab, Cell F46).

3.1.1.2.3.5   Global warming potential values

This dropdown menu allows the user to choose the global warming potential (GWP) and the lifetime to be used in PRELIM. Available values include values from IPCC Fourth Assessment Report (AR4) and IPCC Fifth Assessment Report (AR5) for 20 and 100 years GWP time horizon.

3.1.1.2.3.6   Upstream Releases

This dropdown menu allows users to choose whether they would like to consider the upstream emissions associated with off-site electricity generation and natural gas production/processing. By default, upstream emissions are included in PRELIM.

3.1.1.2.3.7   Off-site Managed Waste Releases

This dropdown menu allows users to choose whether they would like to consider the emissions associated with off-site waste management activities. By default, waste management emissions are included in PRELIM.

3.1.1.2.3.8   Asphalt production

This slider bar tool allows users to control the proportion of liquid heavy ends components (currently sent to marine fuel production) that is used for asphalt production. This option applies to medium and deep conversion refinery configurations. If the configuration is set to `Asphalt Production (10)` via coking refinery `Process unit configuration` dropdown menu, users will be able to increase the amount of asphalt production through the third slider bar that ranges from 0 to 100% of the HVGO being diverted to VR unit.

3.1.1.2.3.9   Off-gas Product Production

Three slider bar tools are provided that allow users to determine if off-gas product production includes LPG, petrochemicals and/or RFG. Note all off-gas product production will be considered as refinery fuel gas and used as energy source within the refinery if there is no LPG, petrochemical feedstock, or RFG production selected.

If the RFG slider is not activated (i.e., set to 0%), it means 1) RFG is consumed onsite either as a fuel or as a feedstock; 2) RFG is primarily used for heating, if there is surplus, it is then used for steam production, followed by hydrogen production; 3) natural gas is then used as a supplement to replenish the refinery's needs for heat, steam and hydrogen; 4) if LPG and petrochemical sliders are not activated (i.e., set to 0%), then all off-gas is assumed to be consumed onsite; if LPG and petrochemical sliders are activated (i.e., 100%), a portion of off-gas is produced as LPG and petrochemical, the remainder is consumed.

If the RFG slider is activated (i.e., set to 100%), it means 1) RFG is produced as a product with its own emissions factor; 2) more natural gas is needed for heat, steam and hydrogen production, which can lead to higher refinery emissions given natural gas is more emissions intensive than RFG (upstream emissions of natural gas, see `Emissions Factors` sheet); 3) if LPG and petrochemical sliders are not activated (i.e., 0%), then all off-gas is produced as RFG; if LPG and petrochemical sliders are activated (i.e., set to 100%), a portion of off-gas is produced as LPG and petrochemical, the remainder is produced as RFG.

3.1.1.2.3.10 Cogeneration of Heat and Power (CHP)

This dropdown menu gives users the option of using cogeneration to supply electricity by selecting a specific CHP technology to use. The available options are: `No Cogeneration Unit`, `Gas Turbine and unfired HNSRG`, `Microturbine`, `Reciprocating Engine`, `Steam Turbine (chemical plant)`, `Fuel cell (PAFC, MCFC commercially available; PEM and SOFC to develop)` or `NGCC-CHP (Gas turbine & Steam Turbine)`. All technologies (except the steam turbine) are assumed to meet the electricity requirement for individual process units. The steam turbine is assumed to meet each process unit's steam requirement.

3.1.1.2.3.11 Region Selection (Jet Only)

This dropdown menu gives users the option of selecting where the refinery is located. Unit yield patterns, intermediate flow split ratios (to downstream units), and utility rates that are associated with jet production are updated for each region using regional average values. The choice of region will update the following items: 1) Straight run Kero split to blending, KHT, and DHT. 2) DHT and Hydrocracker yield ratio to jet blending. 3) yield pattern of some processing units to global average values using proprietary industry datasets, including FCC, Naphtha Reformer.

3.1.2 Main results box

In the `Main Input & Output` worksheet, the `Main results` box displays aggregated results for the selected crude assay in terms of energy use (top left), and environmental impacts assigned to the impact categories included in the US EPA Tool for the Reduction and Assessment of Chemical and Environmental Impacts (TRACI) life cycle impact assessment (LCIA) method (top right), product slate, and energy and TRACI impacts allocated to individual products (bottom). These numbers are re-calculated every time a change is made to the input parameters.

3.1.2.1 Energy use

The `Energy use` section presents all energy commodities (electricity, heat, steam, hydrogen, and refinery fuel gas) used in each of the two major refinery modelling structures for the selected crude oil assay. The unit is MJ of energy consumed/bbl of crude. The energy use table offers a visual comparison of the results for the coking and the hydrocracking refineries.

> Note: a negative hydrogen value indicates a surplus of hydrogen.

3.1.2.2 Environmental Impacts

The `Environmental Impacts` section presents the environmental impacts assigned to each of the TRACI impact categories associated with each of the energy commodities used in each of the two refineries for the selected crude oil assay. For example, the impacts assigned to the Global Warming Potential (GWP) impact category are presented in kg of CO_2e/bbl of crude for the selected refinery configuration.

The `See more results` button links to the `Results Single Assay` worksheet and displays more detailed results for the selected assay.

3.1.2.3   Product slate

The `Product slate` section presents the shares of final products in bbl of product per day (if 100,000 barrels of crude enter the refinery each day and a percentage of total products produced.

3.1.2.4   Energy consumption and environmental impacts by unit of final product

The `Energy consumption and TRACI environmental impacts by unit of final product` section presents the energy and environmental impacts allocated to refinery products in MJ/MJ of final product.

> Note that a zero value for energy or emissions may indicate that the product has not been included in the allocation to products option available in the `Additional inputs and options` (see `Pick allocation products`).

3.1.2.5   Hydrotreater H content sensitivity analysis

The `Hydrotreater H content sensitivity analysis` section presents the effect of changes in hydrotreater output hydrogen content assumptions used for the global hydrogen mass balance on total refinery GHG emissions estimates in PRELIM. The results are presented for both refinery modelling structures.

3.2   Expert Input

The `Expert Input` worksheet allows users to access additional input options. Note the **Excel Solver function needs to be enabled** in order to use expert inputs.

3.2.1   Inputting a custom assay

In the `Input custom assay` section, users can fill in the blue-shaded fields in the blank assay template with the assay's properties. These properties need to be converted into the PRELIM assay format (see section 2.3.2.4 for details on the PRELIM format). Volume flow and API gravity are automatically calculated from the input fields.

This custom assay is automatically copied into the `Assay Inventory` worksheet and can be used in the model by selecting `Use Custom Assay` in the `Main Input & Output` worksheet's dropdown menu.

> Note: The name of the custom assay can be customized by modifying cell `F6` on the `Expert Input` worksheet.

3.2.2   Crude Blender

The `Crude Blender` section displays a table where users can select between 2 and 10 crude oil assays from the assay inventory and specify the amount of each crude in the blend using a mass ratio. Note that each cell in the `Crude Assays` column contains a dropdown menu that contains all available assays.

Clicking the `Create Blend` button then runs a macro (`Blending WeightAverageMethod`) that automatically calculates the properties of the resulting blend on a mass basis. After the user specifies the desired crude oil assays and the desired mass fractions of those crude oils in the final blended assay, the corresponding fractions of the individual crude oil assays selected to be blended are assumed to be mixed and thermodynamic mixing rules are used to calculate the mixture properties and to generate the blended assay. These properties are displayed below as well as in the `Assay Inventory` worksheet in the PRELIM format.

The blended crude assay can be used in the model by selecting `Use Custom Blend` in the `Main Inputs` worksheet's dropdown menu.

3.2.3 Advanced features (Beta version)

In the `Advanced features (Beta Version)` section, the user can access three different product slate optimization procedures and one product slate variation tool as listed below.

- Specify the desired gasoline to diesel ratio in product slate by filling in the blue-shaded fields in `Objective 1: Gasoline and Diesel production ratio` option. The blue boxes in `A- Define shares between gasoline and diesel` allows input of fixed gasoline and diesel production, which is then converted to a ratio. The dropdown menu `B- Assign share` allows the basis of analysis to be selected (i.e., volume or energy basis).
- Specify the desired gasoline share in the product slate by filling in the blue-shaded field in the `Objective 2: Fixed gasoline share in product slate/ share in product slate` option as a percentage on a volume basis.
- Specify the desired product slate by filling in the blue-shaded fields in the `Objective 3: Specific Product slate` option as a percentage on a volume basis (excluding the volume of LPG and petrochemical feedstock).
- Specify the desired volume flow of the crude jet fuel/kerosene fraction that is redirected to the crude diesel fraction via jet-diesel swing (alternative operation mode) for further processing in downstream processes at the refinery.
- Specify the cetane number for hydrotreated diesel and octane number for catalytic naphtha reformer gasoline or reset it to PRELIM default values. If cetane number and/or octane number are manually set, the model will try to match as closely to the set values even when other inputs are changed.

These features are realized by adjusting process unit capacities and redirecting material flows among them. **Optimization results are displayed in a newly generated worksheet without affecting any of the other spreadsheets (changes made in the process of product optimization are reverted). However, users may copy the swing cut settings to the** `CokingRefineryControls` **or** `HydroRefineryControls` **worksheets to investigate the changes**. The options above are included for both refinery modelling structures/calculation sets. In some cases, the user can select the refinery to which it applies using the `run for Coking Refinery` or `run for Hydro Refinery` buttons.

> To use these features, the Solver add-in must be activated, and Solver reference must be available in Excel VBA. The user shall have activated the solver add-in and reference. PRELIM provides instructions on how to manually activate the solver add-in and reference by clicking the `Manual Instructions` button. Also, an `Automatic Activation` button is provided for automatic activation.
>
> Also note that there is a MATLAB app available on the PRELIM website to help with product slate matching.

3.3 Results Single Assay

The `Results Single Assay` worksheet displays results that are updated every time a change is made to an input parameter for the selected crude oil assay based on selected options in the `Main Input & Output`

worksheet. Results are displayed in terms of product slate, energy use, and GHG emissions in a second level of detail:

- Product slate is provided in volume, energy, and mass basis.
- Energy use and GHG emissions are provided on a per bbl of crude oil and per MJ of refinery product basis. A breakdown of the contributions of each type of process energy to energy use and GHG emissions is also provided.

Results are displayed first for the coking refinery (blue headings), then for the hydrocracking refinery (red headings).

Two buttons on the right side of the table link to more detailed results for the coking and hydrocracking refinery, respectively.

3.4 Results All Assays

The `Results All Assays` worksheet displays results for all crude assays available in the `Assay Inventory` worksheet using the appropriate configuration that is chosen based on the criteria described in sections 5.2.2 and 5.2.3 (or selected configuration if it is overridden). This worksheet is updated when the (`Float all assays`) macro is run by clicking the `All assays in inventory` button located in the `Display detailed results` subsection in the `Main Input & Output` worksheet. The macro iteratively calculates, copies, and pastes the results from each assay in this worksheet. When completed, the worksheet displays results for all assays available in the inventory, using the same format and level of detail as the `Results Single Assay` worksheet.

An `Erase results` button in the top left corner of the worksheet allows the user to delete all current results on this worksheet.

> Note: running the macro and displaying this worksheet can take up to 20 seconds depending on your computer's specifications.

3.5 Coking Refinery Detailed Results

The `CokingRefinery Detailed Results` worksheet displays detailed results for the selected crude oil assay using the coking refinery. This worksheet contains three main types of information:

- The `Process Energy Inputs and Outputs` table displays the input and output energy for each of the enabled process units;
- The `Process Life Cycle GHG Emissions` table displays the GHG emissions associated with the energy use of each of the enabled process units; and
- The `Contributors to the coking refinery's GHG emissions` figure presents the distribution of the contribution to GHG emissions per energy source on a process unit basis.

This worksheet is a display-only worksheet and does not offer any interactivity for the user.

3.6 Hydrocracking Refinery Detailed Results

The `HydroRefinery Detailed Results` worksheet displays detailed results for the selected crude oil assay using the hydrocracking refinery. This worksheet contains three main types of information:

- The `Process Energy Inputs and Outputs` table displays the input and output energy for each of the enabled process units;
- The `Process Life Cycle GHG Emissions` table displays the GHG emissions associated with the energy use of each of the enabled process units; and
- The `Contributors to the hydrocracking refinery's GHG emissions` figure presents the distribution of the contribution to GHG emissions per energy source on a process unit basis.

This worksheet is a display-only worksheet and does not offer any interactivity for the user.

Part II Technical documentation: Modelling Methods and Default Specifications

This section provides technical documentation for the calculation and data and constants worksheets to explain how PRELIM works at a detailed level. More specifically, it details the relationship between the worksheets and how PRELIM models the refinery's process units in terms of assumptions, constants, and calculations.

4 Model Overview

Figure 3 presents a simplified process flow diagram of PRELIM structure and how the process units are connected. A total of 11 refinery configurations are available for selection, through two major refinery modelling structures: a coking and a hydrocracking refinery. Generally, PRELIM includes only "major" refinery processes (defined either by installed capacity in North America or by its potential for widespread adoption within the next 20 years) that are related to the **production of transportation fuels**. A detailed process flow diagram for each refinery configuration is available in sections 6.2 and 6.4. Each refinery configuration is modelled at a process unit level, an improvement over current public Well-To-Wheel models (e.g., GREET [Argonne National Laboratory, The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) Model. http://greet.es.anl.gov], and GHGenius [Natural Resources Canada, GHGenius A model for life cycle assessment of transportation fuels. http://www.ghgenius.ca]). The capabilities for more detailed modelling is discussed throughout this section. A material balance connects the different process units along with flow splitters that together simulate different refinery configurations.
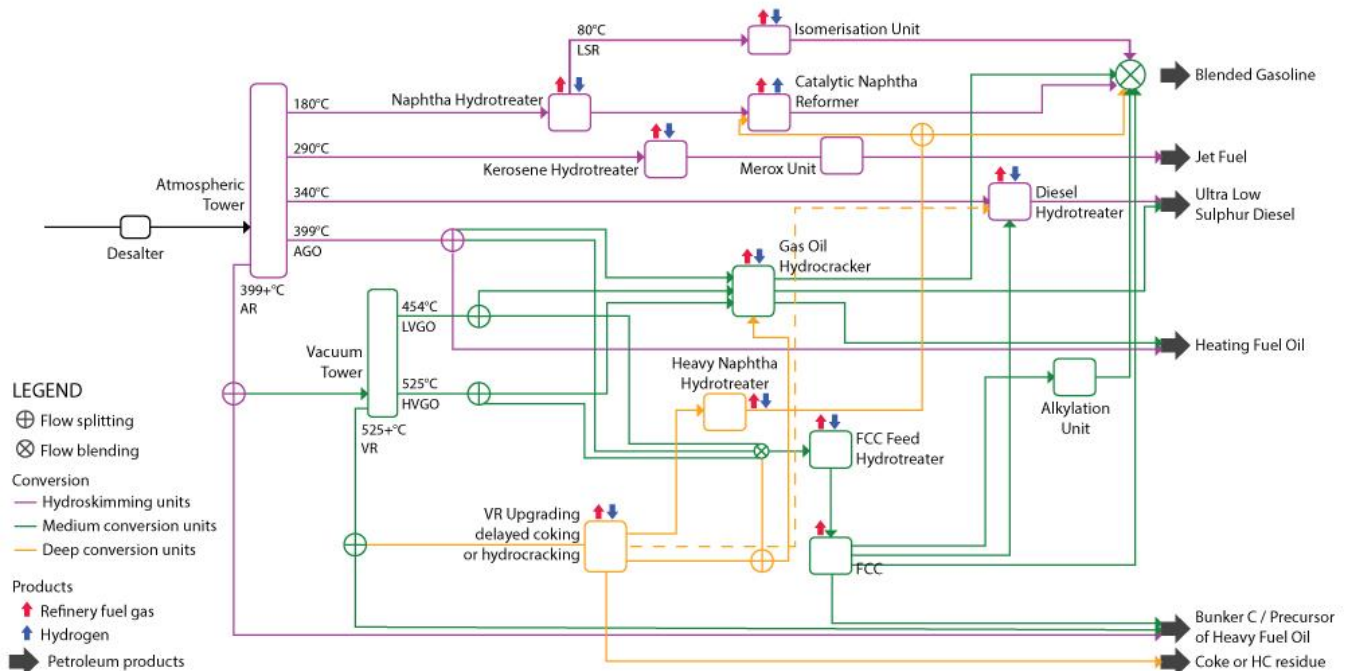
Figure 3: PRELIM simplified process flow diagram

Flow splitters allow for different configurations based on three major refinery categories. The Atmospheric Residue (AR) flow splitter sends AR to the Heating Fuel Oil pool for a Hydroskimming Refinery. Otherwise, it is sent to Vacuum Distillation to simulate other refinery categories (Medium and Deep Conversion Refineries). The Vacuum Residue (VR) flow splitter sends VR to the Fuel Oil pool for a Medium Conversion Refinery or to VR Upgrading for a Deep Conversion Refinery. Atmospheric Gas Oil (AGO), Light Vacuum Gas Oil (LVGO), Heavy Vacuum Gas Oil (HVGO), and Coking or Gas Oil Residue Hydrocracking (GO-Resid HC) split swing cuts send the gas oils either to Gas Oil Hydrocracking or Fluid Catalytic Cracking or to both processes to simulate different types of Medium and Deep Conversion Refineries. Hydrotreated Heavy Naphtha can be sent either to the Naphtha Catalytic Reformer to increase hydrogen production or to the Gasoline pool. Brown dashed lines represent Hydrocracked Diesel intermediate product that is only produced if the VR upgrading uses Residue Hydrocracking, and optional blending of heavy naphtha in the gasoline pool. Abbreviations: Treatment

All configurations (except for the `asphalt configuration`) include atmospheric crude distillation, hydrotreating, and naphtha catalytic reforming process units. The configurations are differentiated by whether a vacuum crude distillation process unit and the following conversion technologies are present: gas oil hydrocracking and/or fluid catalytic cracking (referred to hereafter as FCC); delayed coking or residue hydrocracking. The thermal cracking technologies (e.g. FCC and delayed coking) increase the hydrogen to carbon ratio through carbon rejection while the hydrocracking technologies (gas oil and residue hydrocracking) modify the hydrogen to carbon ratio by adding hydrogen produced through a separate process unit (steam methane reforming referred to hereafter as SMR).

Each configuration requires a different amount of energy to process a crude and produces a different slate (i.e., volume and type) of refinery final products including transportation fuels (i.e., gasoline, kerosene, and diesel) as well as heavy fuel oil, hydrogen from the naphtha catalytic reforming process, refinery fuel gas (i.e., gas produced as a by-product in process units within the refinery), and the possible production of coke or hydrocracking residue. Liquefied Petroleum Gas (LPG) and petrochemicals are alternative final products in refineries, and they are modelled in a simplified way in the current version of PRELIM (section 5.3.4).

For each process unit, the model calculates the energy that it requires and predicts the quantity and destination of products exiting the process unit using the following data: process unit energy requirements, process unit intermediate product yields, intermediate product characteristics (API, sulphur, and hydrogen content), and crude assay information. PRELIM also calculates the upstream energy use and GHG emissions associated with the energy sources (i.e., electricity and natural gas) (Baumann et al., 2004). Fugitive GHG emissions from the refinery tend to be an order of magnitude lower than combustion emissions (EPA, 2009) and are not considered in the current version of PRELIM.

PRELIM can calculate overall refinery energy and environmental impacts (TRACI) on per barrel of crude or per megajoule (MJ) of crude bases as well as for a final product on a per MJ of product basis (e.g., per MJ of gasoline). For the latter type of functional unit, an allocation process of the energy use (amount and type) occurs at the refinery process unit level. That is, at each process unit, the amount and type of energy used is allocated to the process unit throughputs. In the next process unit, the sum of the energy embedded in the process feed (calculated by the allocation in preceding processes) and energy used in that process unit is similarly allocated to the process unit throughputs. Energy use and type of energy are traced through the entire refinery to the final products (Wang et al., 2004). PRELIM allows the flexibility to choose which products are assigned emissions (e.g., to transportation fuels only, transportation fuels plus coke) as well as the basis of allocation (i.e., hydrogen content, mass, market value, or energy content basis). Comparison of overall energy requirements in the refinery (calculated by adding the embedded energy in all the refinery final products which account for process unit throughputs on a mass unit basis) versus total energy requirements from all process units verifies the energy and material balance in the system.

To run the model, users must select a crude, a configuration, and an allocation method desired. Default values can be used to represent the crude properties (by selecting a crude from the crude assay inventory in the model) and process units. Alternatively, users can import a new crude assay or can modify any of the model parameters either by selecting a value in the range of values available in the model for each parameter or by inputting their

own parameter value(s). To characterize the whole crude and its fractions, a total of 62 parameters are imported into PRELIM, accounting for five crude oil quality properties: crude distillation curve (i.e., information in terms of mass and volume yields of each fraction, and single fraction characteristic boiling point), API, sulphur content, hydrogen content as well as carbon residue Table 8 highlights the parameters). Two additional crude properties (aromatic content and crude light ends content) impact refinery GHG estimates and are modelled indirectly in PRELIM (sections 5.3.2, 5.3.4, and 5.5.7).

4.1 Data Sources

Unless specified in the model or the documentation, PRELIM uses the following sources for default values, calculations, and equations:

- Gary, J.; Handwerk, G.; Kaiser, M., Petroleum Refining Technology and Economics Fifth ed.; CRC Press: New York, 2007.
- Parkash, S. Refining Processes Handbook, Burlington: Elsevier, 2003.

A complete list of references used to build, document, and validate the PRELIM model is available in section 6.2.2.

Process unit energy requirements in PRELIM are presented with both default values and possible ranges derived from the literature. The data were compared with confidential information and evaluated in consultation with industry experts to verify the values and their ranges are appropriate. Having said this, process energy requirements can vary greatly from refinery to refinery. Therefore, the user can override the data in the `Constants` worksheet to reflect a specific refinery or scenario.

Some cells in the calculation worksheets include comments to explain calculations or provide the user with a source. Cells that are commented typically display a red triangle in their top right corner.

> Note: you may need to activate the comment display option in Microsoft Excel to be able to display comments.

5 Modeling Methods

A refinery is defined as a set of interconnected process units that convert relatively low value hydrocarbon materials into more valuable products by increasing their hydrogen to carbon ratios. PRELIM can simulate up to eleven specific refinery configurations. Calculations for all configurations are structured within the arrangement of and relations between the process units of two major refinery configurations: coking refinery and hydrocracking refinery (also called hydro refinery). The set of calculations in each of these two major refineries include calculations for several common processes among configurations and for alternative medium conversion processes (i.e., gas oil hydrocracking and fluid catalytic cracking). They differentiate themselves by the specific calculations to model either the delayed coking or the residual hydrocracking process units; both are deep conversion mutually exclusive processes that interact in different ways with other process units and yield different products.

5.1 Calculations

The calculation worksheets are where most, if not all, of the calculations take place using specific modeling methods at both a process unit and a system level. For each of the two refinery modeling structures/calculation sets in PRELIM (i.e., CokingRefinery and HydroRefinery), three types of calculations worksheets have been created:

1. The Process flow diagram worksheets (`CokingRefineryPFD` and `HydroRefineryPFD`)
2. Calculation worksheets (`CokingRefineryCalcs` and `HydroRefineryCalcs`)
3. Control worksheets (`CokingRefineryControls` and `HydroRefineryControls`)

The general modeling methods used to structure PRELIM calculations within each of these worksheets are described as follows.

5.2 Process Flow Diagrams

The `CokingRefineryPFD` and `HydroRefineryPFD` worksheets or process flow diagram (PFD) worksheets present the general flow and relationship between the refining technologies included in the refinery configurations modeled in PRELIM. The PFDs display the material flow of feedstock, intermediate products, and final products between the process units as well as results for key performance indicators including volumetric flow rate feed and total process energy requirement by energy source for each process unit (calculated in the calculations worksheets).

The `CokingRefineryPFD` and `HydroRefineryPFD` worksheets' purpose is two-fold:

1. Use Excel IF functions to return material and energy flow values for enabled process units through the modeling conditions defined with the refinery configuration set of options from the `Main Input and Output` worksheet and with advance modeling options developed in the control worksheets; modeling options are on the upper left side of the worksheet and grouped in a `Process Flow Diagram` box.
2. Use Excel IF function to perform intermediate and final allocation calculations for the process unit allocation method defined in the `Main Input and Output` spreadsheet; modeling options are on the upper left side of the worksheet and grouped in the `Process Flow Diagram` box.

> A box at the top left of the PFD worksheets sum up the currently enabled configuration. Note that the box on the CokingRefineryPFD worksheet contains configuration options that apply to both refineries.

5.2.1   PRELIM Refinery Configuration

Every refinery is configured differently, and every crude can be processed in a range of refinery configurations. The interconnection of process units adopted in PRELIM (Figure 3) is consistent with many general energy petroleum refinery flow structures (see for example Robinson (2006), Energetics (2007), Wiley (2007), and Gary et al. (2007) for refinery configuration representations and for general to detailed descriptions of refinery processes and their interconnections). For the purposes of obtaining a generalized tool, the configuration is simplified based on discussions with refinery operation experts. For example, PRELIM assigns a default hydrotreating process unit either prior to or after the FCC unit. Refineries can meet gasoline sulphur content specifications either by using a hydrotreating process unit of FCC feedstock (hydrotreating of heavy gas oil) or a hydrotreating process unit of FCC gasoline product (gasoline desulphurization). Each of these process units is present in 39% of U.S. refineries, and their installed capacities are comparable (Table 3). A second example is that the current version of PRELIM does not model interflows of intermediate products among FCC, delayed coking, and hydrocracking process units. (e.g., FCC processing heavy material derived from the gas oil hydrocracking process unit [Robinson, 2006], hydrocracking or delayed coking processing medium to heavy fractions derived from the FCC process unit [Gary et al., 2007]). However, processing of recycled intermediate products among these process units is only in operation in 17% of U.S. refineries (EIA, 2008) and the installed capacity of process units to process such recycled feed is low (Table 3).

Table 3: Capacities of the major refining processes in U.S. petroleum refineries and distribution as share of atmospheric crude distillation capacity

Refinery Process	Downstream Charge Capacity (BPSD)[a]	Distribution Share of Crude Distillation Unit capacity	Included within PRELIM
Atmospheric Crude Oil Distillation	18,581,089	100.0%	Yes
Vacuum Distillation	8,542,643	46.0%	Yes
Thermal Cracking	2,631,676	14.2%	
Thermal Cracking, Coking	2,605,076	14.0%	
Delayed Coking	2,500,676	13.5%	Yes
Fluid Coking	104,400	0.6%	No
Thermal Cracking, Visbreaking	16,000	0.1%	No
Thermal Cracking, Other (including Gas Oil)	10,600	0.1%	No
Catalytic Cracking, Fresh Feed	6,140,121	33.0%	Yes
Catalytic Cracking, Recycled Feed	91,840	0.5%	No
Catalytic Hydrocracking	1,819,700	9.8%	
Catalytic Hydrocracking, Distillate	595,200	3.2%	Yes
Catalytic Hydrocracking, Gas Oil	1,079,500	5.8%	Yes
Catalytic Hydrocracking, Residual	145,000	0.8%	Yes
Catalytic Reforming	3,700,463	19.9%	Yes
Catalytic Reforming/Low Pressure	2,322,700	12.5%	
Catalytic Reforming/High Pressure	1,377,763	7.4%	

Refinery Process	Downstream Charge Capacity (BPSD)[a]	Distribution Share of Crude Distillation Unit capacity	Included within PRELIM
Desulphurization (including Catalytic Hydrotreating)	16,023,206	86.2%	
Catalytic Hydrotreating, Naphtha/Reformer Feed	4,281,046	23.0%	Yes
Desulphurization, Gasoline	2,394,882	12.9%	Yes[b]
Catalytic Hydrotreating, Heavy Gas Oil	2,796,798	15.1%	Yes
Catalytic Hydrotreating, Distillate	5,676,032	30.5%	
Kerosene/Jet Fuel	1,339,150	7.2%	Yes
Diesel Fuel	3,647,211	19.6%	Yes
Other Distillate Fuel	689,671	3.7%	
Catalytic Hydrotreating, Other/Residual Fuel Oil	874,448	4.7%	
Residual Fuel	246,200	1.3%	No
Other Oils	628,248	3.4%	No
Fuels Solvent Deasphalting	383,250	2.1%	No

[a] BPSD: Barrels Per Stream Day. It is the maximum number of barrels of input that a refinery can process within a 24-hour period, running at full capacity under optimal conditions, with no allowance for downtime.

[b] Naphtha and gas oil hydrotreating fulfill gasoline desulphurization requirements.

Source: U.S. Energy Information Administration Data at January 1st, 2010.

5.2.2 CokingRefinery PFD – Configurations available

Figure 4 displays the coking refinery PFD as modeled in PRELIM. A PFD for each configuration is available in section 6.2 for all configurations common to both refinery modelling structures and in section 6.3 for configurations specific to the coking refinery.
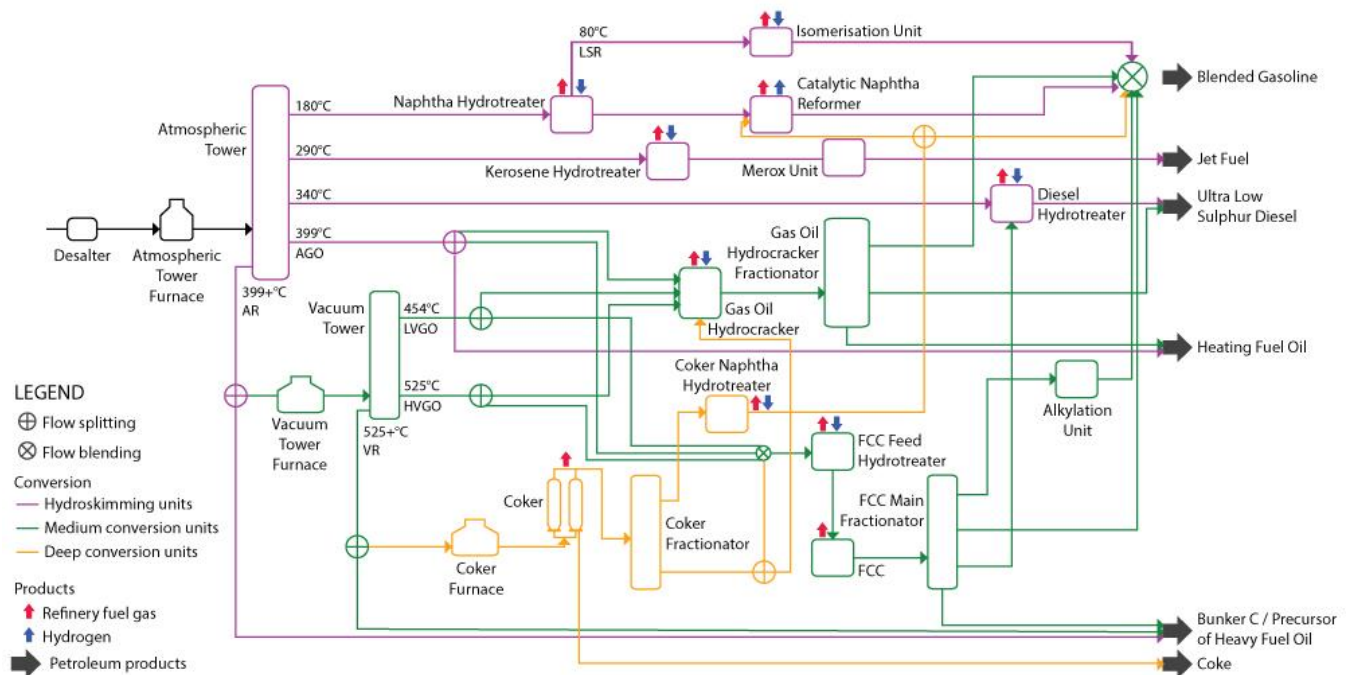
Figure 4: Coking refinery process flow diagram in PRELIM

The coking refinery modeling structure consists of 21 process units that are enabled or disabled depending on the selected configuration. All refinery configurations include crude distillation, hydrotreating, and naphtha catalytic reforming processes. The configurations can be categorized in three types:

- The **hydroskimming** configuration is a basic configuration that processes the crude oil from the atmospheric tower into refined products without additional transformation (units in purple in Figure 3) (configuration 0).
- The **medium conversion** configuration comprises the hydroskimming process units but also processes the heaviest component of the stream further using additional process units (units in green in Figure 3). The medium conversion can be run using one of these three configurations:
  - Using the fluid catalytic cracking only (configuration 1);
  - Using the gas oil hydrocracker only (configuration 2); or
  - Combining the fluid catalytic cracking and the gas oil hydrocracker (configuration 3).
- The **deep conversion** configuration includes additional process (e.g., coker) units to the medium conversion configuration, allowing for further processing of the heaviest fraction exiting the bottom of the atmospheric tower using higher temperatures to crack heavier compounds into higher quality products (units in orange in Figure 3). The deep conversion configuration can be run using one of these three configurations:
  - Using the fluid catalytic cracking only (configuration 4);
  - Using the gas oil hydrocracker only (configuration 5); or
  - Combining the fluid catalytic cracking and the gas oil hydrocracker (configuration 6).
- The **asphalt production** consists of only the desalter, the atmospheric furnace and tower, and the vacuum furnace and tower. Currently, PRELIM assumes that for this configuration all products from both towers are not further treated and are sold as is (i.e. no refined products are made). Therefore, the properties and compositions of all output streams from the atmospheric tower remain unchanged.

In the coking refinery modeling structure/calculation set, the three configurations are not independent. Modelling of the medium conversion includes calculations of the hydroskimming configuration, and modelling of the deep conversion requires both the hydroskimming and medium conversion process unit calculations.

A default refinery configuration is assigned for each crude oil assay, using API gravity and sulphur content of the whole crude as the criteria. Figure 5 illustrates how PRELIM determines the most suitable configuration to process the crude among configurations 1, 3, 6, or 9.

PRELIM cannot automatically assign configurations 2, 4, 5, 7, 8 and 10 based on its current selection criteria. That is, the medium conversion always uses configuration 3, and the deep conversion uses configuration 6 for the coking refinery and configuration 9 for the hydrocracking refinery. These configurations have both the fluid catalytic cracker and the gas oil hydrocracker enabled. The user can override these selections to explore the impact of using one of the other refinery configurations that are available.

Users can override the default configuration and pick another one in the `Process unit configuration` option available through a drop-down option list in the `Main Input & Output` worksheet.
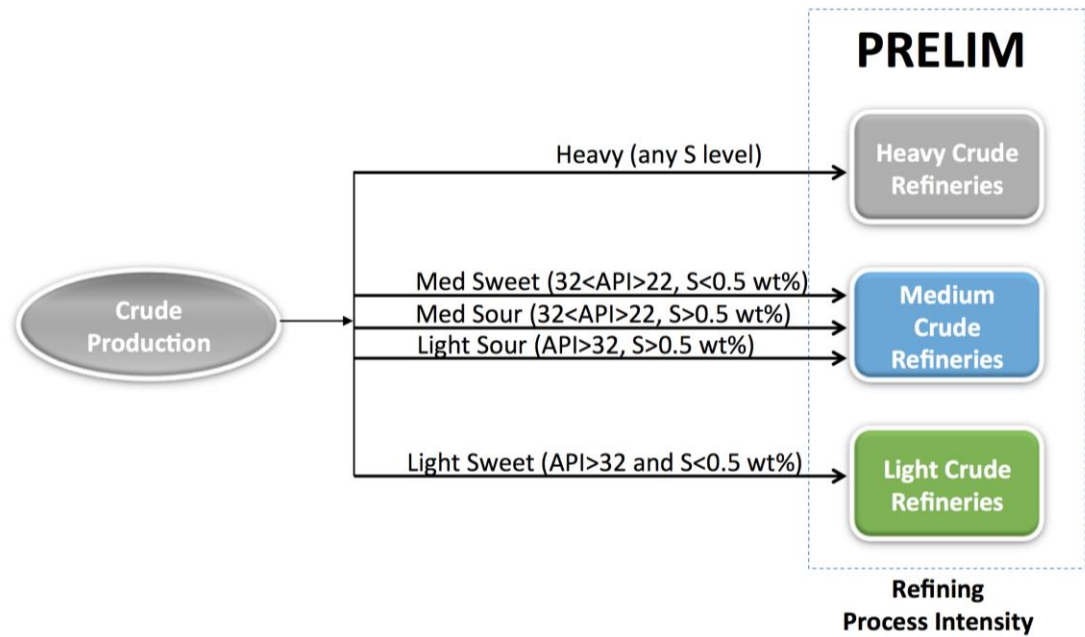
Figure 5: How PRELIM determines the refinery default configuration

5.2.3 Hydrorefinery PFD - Configurations available

Figure 6 displays the hydrocracking refinery PFD as modeled in PRELIM. A PFD for each configuration is available in section 6.2 for all configurations common to both refinery modelling structures and in section 6.4 for configurations specific to the hydrocracking refinery.

The hydrocracking refinery consists of 21 process units that are enabled or disabled depending on the selected configuration. All refinery configurations include crude distillation, hydrotreating, and naphtha catalytic reforming processes. The configurations can be categorized in three types:

- The **hydroskimming configuration** is a basic configuration that processes the crude oil from the atmospheric tower into refined products without additional transformation (units in purple in Figure 6) (configuration 0).
- The **medium conversion** configuration comprises the hydroskimming process units but also processes the heaviest component of the stream further using additional process units (units in green in Figure 6). The medium conversion can be run using one of these three configurations:
    - Using the fluid catalytic cracking only (configuration 1);
    - Using the gas oil hydrocracker only (configuration 2); or
    - Combining the fluid catalytic cracking and the gas oil hydrocracker (configuration 3).
- The **deep conversion** configuration includes additional process units (e.g., residue hydrocracker) to the medium conversion configuration, allowing for further processing of the heaviest fraction exiting the bottom of the atmospheric tower using higher temperatures to crack heavier compounds into higher quality products (units in orange in Figure 6). The deep conversion configuration can be run using one of these three configurations:
    - Using the fluid catalytic cracking only (configuration 7);
    - Using the gas oil hydrocracker only (configuration 8); or
    - Combining the fluid catalytic cracking and the gas oil hydrocracker (configuration 9).

In the hydro refinery modeling structure/calculation set, the three configurations are not independent. Modelling of the medium conversion includes calculations of the hydroskimming configuration, and modelling of the deep conversion requires both the hydroskimming and medium conversion process unit calculations.
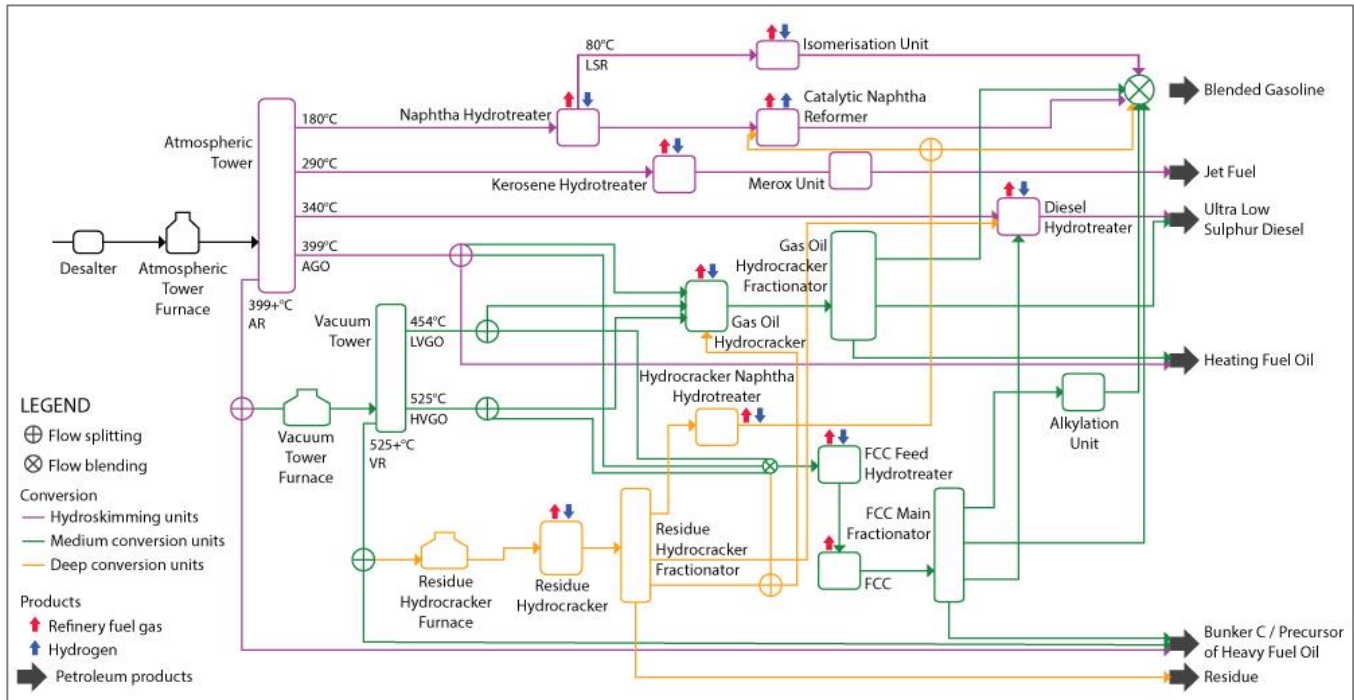
Figure 6: Hydrocracking refinery process flow diagram in PRELIM

The method used to determine the default refinery configuration is similar to the one used for the coking refinery and is explained in the previous section. Users can override it and pick another configuration in the `Process unit configuration` option available in the `Main Input & Output` worksheet.

5.2.4 Calculations for allocation of energy and greenhouse gases

PRELIM can calculate overall refinery energy use and GHG emissions on a per barrel of crude or per megajoule (MJ) of crude basis, and on a per MJ of product basis (e.g. per MJ of gasoline). For the latter type of functional unit, an allocation process of the energy use (amount and type) occurs at the refinery process unit level. That is, at each process unit, the amount and type of energy used is allocated to the process unit throughputs. In the next process unit, the sum of the energy embedded in the process feed (calculated by the allocation in preceding processes) and energy used in that process unit is similarly allocated to the process unit throughputs. Energy use and type of energy are traced through the entire refinery to the final products (Wang et al., 2004). PRELIM allows the flexibility to choose which products are assigned emissions (e.g., to transportation fuels only, transportation fuels plus coke) as well as the basis of allocation (i.e., hydrogen content, mass, market value, or energy content basis). All the required calculations associated to this allocation process are included in the `CokingRefineryPFD` and `HydroRefineryPFD` worksheets. A comparison of overall energy requirements in the refinery (calculated by adding the embedded energy in all the refinery final products which account for process unit throughputs on a mass unit basis) versus total energy requirements from all process units verifies the energy and material balance

in the system. The verification is conducted in the `CokingRefineryCalcs` and `HydroRefineryCalcs` worksheets.

5.3 RefineryCalcs

The `CokingRefineryCalcs` and `HydroRefineryCalcs` worksheets are where most of the material balance and energy requirement calculations take place. PRELIM models the mass and volumetric flow rates, the energy use and requirement of each of the process units of the refinery in these worksheets. Each worksheet has two boxes:

- The `Process unit level calculations` box details all calculations for each process unit; and
- The `System-level calculations` box displays results aggregated at the refinery level.

The calculations involve the following steps:

1. Estimate total process energy requirements based on process unit energy intensity values;
2. Carry out hydrogen mass balances at the hydrogen addition process units and at the refinery level;
3. Estimate intermediate and final product yields for each process unit;
4. Conduct energy and GHG emissions allocation of primary energy carriers (e.g., allocated hydrogen in PDF worksheets is translated into allocated fuel gas, steam, electricity, and feedstock in the calculation worksheets) and verify the energy and material balance in the system.

The refinery calculations are based on a set of default specifications and constants derived from peer-reviewed literature (as described in sections 4.1 and 5). The main default specifications and constants used in the calculations are highlighted with a red background in the calculations worksheets and can be overridden by expert users directly in the cells or via the `Constants` worksheet.

The calculations also account for PRELIM swings modeling information. By default, for a selected refinery configuration, PRELIM assumes that interflows among process units and intermediate product slates from each process unit are all fixed. Swings, also known as flow splitters, can redistribute flows between process units based on user's commands to customize the final refinery-level product slate. These swings are defined by the refinery configuration set of options from the `Main Input and Output` worksheet and the advance features from the `Expert Input` worksheet developed in the Controls worksheets (`CokingRefineryControls` and `HydroRefineryControls`).

5.3.1 Process energy requirements and default specifications

Refinery process units require electricity, heat, and steam (referred to hereafter as "process energy requirements"). Electricity can be purchased from the power grid or produced on site at the refinery. Heat and steam can be obtained by process heat recovery and heat integration systems. The most common system uses pumparound of effluent streams for feed/effluent heat exchanging and/or for steam generation. Fuel gas produced on site and/or natural gas supply the process energy requirements after heat integration. Refineries also may burn fuel oil if the equipment is available and air emissions regulations permit it.

PRELIM calculates total process energy requirements using information from the crude distillation curve (i.e., distribution of the whole crude material into its fractions).

For the distillation process units, two types of energy requirements are calculated: 1) energy for feed preheating, and 2) energy for crude separation (steam requirement). The energy to preheat the distillation process units feed is calculated based on a balance of enthalpies using a correlation from Moharam et al. (1998) for characterization of enthalpy of the crude fractions. The enthalpy of each crude fraction is calculated based on the input and output temperatures of the preheater; the input temperature is assumed to be previously increased by a pumparound system while the output temperature is associated with the operating condition (both temperatures are key parameters in the model (`Constants` worksheet) and can be changed by the user). Moharam et al.'s correlation is recommended (that considers the API and characteristic boiling point of a crude fraction) for light and medium crude fractions (naphtha to gas oil fractions), but it is applied across all fractions in PRELIM. For the light and medium fractions, an average standard deviation of ±2.5% is expected (Moharam et al., 1998). The error of using the correlation for heavier fractions is unknown. However, the correlation helps to differentiate energy requirements for feed preheating among crudes. To the knowledge of the authors, there is no empirical correlation or simple method (based on little input data or commonly available parameters) that could be used for this purpose. Moharam et al. also suggests that more complex correlations will not necessarily be more accurate for the prediction of the enthalpy properties of petroleum fractions (Moharam et al., 1998). In addition, the estimate of the error in the energy estimates for the crude distillation process unit is overestimated in this model in comparison with an industry accepted proprietary model (Baker & O'Brien). Though, it would be expected an accelerated growth in the heat capacity for heavy fractions above what is estimated for the lighter fractions. This implies that the use of the correlation is a conservative calculation in the model. Further work could improve the representation of energy requirements associated with the heavier fractions. The energy required to separate the crude into its fractions is calculated based on the volume of each crude fraction that is produced. The default values for the energy required for separation (the amount of steam per volume of crude fraction produced; input parameters in the model) is informed by industry experts (and literature presented in Table 3) and implies the energy efficiency in the distillation process unit (see Table 3).

Table 4: PRELIM default process energy requirements

Data are given on a per barrel of process unit volume feed basis unless otherwise specified (Szklo et al., 2007).

Refinery Process	Fuel (LHV) MJ/bbl	Electricity kWh/bbl	Steam [a] Lb/bbl	Calculated Energy PRELIM [b] MJ/bbl	Estimated Range U.S.2007 MJ/bbl [i]
Desalting	-	1.5×10^{-2}	-	5.4×10^{-2}	$3.6\text{-}7.2 \times 10^{-2}$ [ii]
Atmospheric Distillation	57 - 67[c]	0.9	4.4 - 8.8[d]	67 - 85	87 - 196
Vacuum Distillation	32 - 42[c]	0.3	0.8 - 10.8[d]	34 – 60	54 - 119
Hydrotreating [e,f] H make-up Scf/bbl					64 - 173
<150	105	2.0	6.0	122	
150-400	158	3.0	8.0	182	
>400	211	6.0	10.0	249	
Naphtha Catalytic Reformer [e]	317	3.0	30.0	317	225 - 361
Isomerization (Isopentane/Isohexane)		1.0	211.0	343	108 - 249
Merox Unit	-	0.1	-	0.36	
Gas Oil Hydrocracker [e,g] H make up (Scf/bbl)					168 - 339
<2000	106	8.0	50.0	216	
2000 – 3000	311	13.0	75.0	480	
>3000	217	18.0	100.0	445	
Fluid Catalytic Cracking [e]	106	- [h]	- [h]	106	221
Alkylation (H₂SO₄)	0	4.1	179.0	306	348 - 359
Delayed Coking	148	30.0 kWh/t coke [i]	5.0lb/bbl coker GO [j]	162 - 176	120 - 243
Steam Production [a,e]	3,502/t steam	4.8/t steam	186/t steam		
Amine Gas Treating [k]	280/m³A	2.6/m³ A	-		
Claus Sulphur Recovery [l]	-	98/t S	-1,215/t S		
Claus Tail Gas Treatment [l]	-	463/t S			
Steam Methane Reforming [m] Estimated energy efficiency					66–167/kgH
62% efficiency	203/kg H	0.33/kg H	-	204/kg H	
91% efficiency	183/kg H	0.20/kg H	-27/kg H	139/kg H	

[i] Energetics. *Energy and Environmental Profile of the US Petroleum Refining Industry* Prepared by Energetics Incorporated Columbia, Maryland for U.S. Department of Energy Industrial Technologies Program: November 2007; pp 39,40.

[ii] Worrell, E.; Galitsky, C. *Energy efficiency improvement and cost saving opportunities for petroleum refineries.*; LBNL-56183; Ernest Orlando Lawrence Berkeley National Laboratory: 2005; pp 10-16.

Base Case refinery energy requirements for processing a crude and GHG estimates are based on data given in Table 4. Most data are obtained from Gary et al. (2007); however, discussion of the data with refinery experts and comparison with confidential data and other literature sources was used to supplement or modify some values:

[a] Gary et al. (2007) suggest a steam LHV 2.79 MJ/kg (1200 Btu/lb) of steam. Refineries produce steam of different qualities using different energy efficiencies. In this study, it is assumed energy consumption to produce high pressure (900 psig) steam. It is high energy demand to produce steam of higher LHV (3.59 MJ/kg; 1542 Btu/lb); however, a high energy efficiency of 85% is also assumed (Parkash, 2003).

[b] No energy consumption for cooling systems is included. The ranges of total calculated energy in distillation and delayed coking process units are for the crudes included in this study.

[c] Atmospheric and vacuum distillation's furnace duty is a function of crude API and of the amount of products or fractions to distillate. PRELIM uses a correlation from Moharam et al. (1998) to determine enthalpy of petroleum fractions based on temperature, crude fraction API and Tb point (see below Approximated Watson characterization factor). This study assumed heating the feed of atmospheric distillation from 288-399 °C (stream of reflux and distillation product streams are used to preheat a desalted crude, see note d), and the feed of vacuum distillation (i.e. atmospheric residuum) from 399-454 °C. Though theoretical calculations of this energy requirement are considered low in comparison to real distillation energy consumption (Energetics. *Energy Bandwidth for Petroleum Refining Processes*; Prepared by Energetics Incorporated for the U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Industrial Technologies: 2006; p 17.), the correlation is used to reflect differences on energy requirements due to crude quality; however, this is an approximation since the correlation is derived from a light fractions' data base (20).

[d] Atmospheric and vacuum distillation stripping steam depends of the boiling range of the feed and the type of fraction to vaporize; Gary et al. (2007) suggest a range of 10 to 50 lb/bbl of feed. PRELIM assumes 6, 4, 2, and 10 lb/bbl for Kerosene, Diesel, AGO, and AR fractions respectively at the Atmospheric distillation, and 15 lb/bbl for VR fraction at the Vacuum Distillation.

[e] Process energy exports can be expected as Energetics (2007) reported for U.S. Refinery industry. This study uses data from Gary et al. (2007) which does not show such values; therefore, there is not credit in this study for that. Besides that, process total calculated energy use is among the U.S. industry range (Energetics. *Energy and Environmental Profile of the US Petroleum Refining Industry* Prepared by Energetics Incorporated Columbia, Maryland for U.S. Department of Energy Industrial Technologies Program: November 2007; pp 39,40). (See note h for FCC unit).

[f] Gary et al. (2007) suggest that hydrotreating energy requirements vary based on hydrogen consumption. Data are available for consumption of the following ranges: 100-150, 150-400, 400-800 scf H/bbl. Hydrogen consumption for each case is determine by global hydrogen mass balance as difference in hydrogen content of hydrotreating feed and products and a factor for hydrogen losses. Additional hydrogen requirements are estimated for sulphur removal. PRELIM's hydrogen consumed for desulphurization reaction is based on stoichiometric quantities to transform sulphur into H2S.

[g] Gary et al. (2007) suggest that hydrocracking energy requirements vary based on hydrogen consumption. Data are available for consumption of 1000, 2000, and 3000 scf H/bbl. In this study, 80% of electricity requirements are allocated to reactor and the other 20% to fractionators. Also, hydrogen requirements in PRELIM application are derived from assuming a hydrocracking severity of 1500 scf H/bbl.

[h] FCC regenerator produces flue gas of important embodied energy. Gary et al. (2007) give data of power consumption of 6.9 kWh/bbl accounting for electric drive for air blower and off gas compressors and does not provide steam consumption data taking into account that FCC usually generates excess of steam by approximately 30 lb of steam per bbl of feed. Refiners may utilize the flue gas to drive a gas expander turbine that could generate the required power for the air blower and

to allow export of electricity. This study assumes that there is not steam export, and that the embodied energy content of the flue gas supplies the steam and electricity demand of the FCC.

[i] PRELIM uses an additional 0.5 kWh/bbl total coker liquids.

[j] Stripping steam depends of the boiling range of the feed and the type of fraction to vaporize. Gary et al. (2007) give a steam consumption of 700 lb/t of coke. PRELIM uses 5 lb/bbl coker gas oil; it is equivalent to 9.5 to 924 lb of steam/t coke for the assay inventory in this study.

[k] Energy requirements are based on amine solution circulation (A). The amine solution circulations is estimated assuming amine ratio of 3.0 moles amine per mole H2S, 100% H2S absorbed in amine, and 20% wt solution (Jones et al., 2008). Gary et al. (2007) give fuel requirements to obtain steam of low pressure (60 psig) for this process unit.

[l] Gary et al. (2007) give energy requirements as function of sulphur recovered. The authors suggest exports of steam of low-pressure steam (250 psig) for the sulphur recovery process unit. In this study, it is assumed high pressure (900 psig) steam (3.59 MJ/kg; 1542 Btu/lb) (see note a); however, for consistency, in this process unit, steam is assumed to have an enthalpy of 2.79 MJ/kg (1200 Btu/lb).

[m] Energy requirements for the production of hydrogen via steam methane reforming (SMR) are given in a per kg of hydrogen basis. Fuel requirement includes natural gas used as feedstock and fuel. Estimated energy efficiency is calculated as the ratio between energy content in hydrogen and SMR process net energy requirement (i.e. fuel requirements for heating, steam production, and electricity plus energy content of natural gas used as a feedstock minus energy content of excess of steam produced). This study uses data from Gary et al. (2007) and NETL report (NETL *Development of Baseline Data and Analysis of Life Cycle Greenhouse Gas Emissions of Petroleum-Based Fuels* DOE/NETL-2009/1346.; National Energy Technology Laboratory: 2008.) as good approximations to current average industry practices (base case) and the case where modern purification technology is used (scenario of improvement of SMR process unit) respectively. Both studies supply the data in energy units and per scf or kg of H basis. This study used GREET version 1.8c default assumptions for fuel specifications; therefore, energy efficiencies were calculated using hydrogen low heating values (LHV) on mass basis: 127.06 MJ/kg and density 2.55 g/ft3. Different assumptions lead to a different estimated energy efficiency (see NETL 2008 report for a range of reported energy use in SMR in the literature and vendors, also NERL (Spath et al., 2001) for different assumptions about hydrogen specifications and energy requirements).

For other process units in the model (e.g., hydrotreating, naphtha catalytic reforming, and SMR process units), PRELIM uses information about the quantity and type of energy required from an individual refinery process unit and assumes that the process energy requirement is linearly related to the process unit volume feed flow. This reflects the process unit level approach that allows the flexibility to scale requirements up and down depending on the quality of the crude. This approach is needed to reflect differences in refining crudes with different distillation curves, which determine the subsequent process unit feed flows, and therefore the processing capacity and energy requirements for each subsequent process unit. This approach coincides with the idea that energy use in refineries is driven by the volume of material processed (Szklo et al., 2007). However, it only represents the case where processing the crude fractions and their derived intermediate products is not constrained by the size or installed capacity of individual processes. Using this approach, energy-intensity (in terms of energy use per barrel of input crude) will be a differentiator in the refinery energy use and GHG emissions estimates for a crude. PRELIM could be modified to reflect process unit capacity constraints but is not included in the current version of the model.

For the purposes of transparency and completeness, the data available in the model for process energy requirements is presented as a range of plausible values derived from the literature (see Table 5). The ranges of process energy requirements are wide in particular for hydroprocessing and the FCC process (e.g., 106 to 498 MJ of fuel/bbl in hydrocracking; 0 to 34 MJ of fuel/bbl in FCC). The data are compared with confidential information

and discussed with experts from industry to conclude that such values and their ranges are feasible. The ranges in fuel and steam requirements arise from desired product yields and heat integration systems (see operation of delayed coking or FCC Catalyst regeneration in section 5.3.3 for examples). The range of electricity required by a unit is associated with its operating conditions and layout. For example, for a hydrotreating process unit, the range of plausible electricity requirements is wide due to variability in pressure, hydrogen consumption, and whether the makeup compressors are onsite or offsite (Karpe, 2010).

Table 5: Range of energy requirements from literature

Process Unit	Hydrogen kg/bbl[a]	Fuel Gas MJ/bbl	Electricity MJ/bbl	Steam MJ/bbl[b]	Source
Desalting			0.00720 - 0.216		[1,2]
Atmospheric Distillation		52.9-95.3	1.80-3.24	16.1-40.7	[1,2]
Vacuum Distillation		31.8-95.3	1.08	16.1-81.4	[1,2]
Hydrotreating					[1,2,3]
Naphtha	0.0602-0.337	0.0491-105	4.32-7.20	9.77-45.6	
Kerosene	0.0602-1.34	159-240	6.12-10.8	4.23-13.0	
Diesel	0.120-0.963	34.8-158	6.12	11.1	
Gas Oil	0.241-2.17	35.8-212	3.24-21.6	11.7-16.3	
Fluid Catalytic Cracking		0.00-105	2.70-7.67	4.70-17.3	[1,2,3]
Alkylation			10.1-39.6	58.6-293	[1,2,3]
Gas Oil Hydrocracking	2.41-7.22	106-498	12.2-64.8	81.4-163	[1,2,3]
Delayed Coking		114-178	4.32-13.0	-29.6-65.1	[1,2,3]
Naphtha Catalytic Reforming		2.64-286	2.16-10.8	48.8-65.1	[1,2,3]
Isomerization	0.0963	190	2.88-3.60	0.00-94.1	[1,2]
	MJ chemical feedstock/kg H_2	MJ/kg H_2	MJ/kg H_2	MJ/kg H_2	
Steam Methane Reforming	97.8-139	16.3-102	0.777-1.26	(0.0505)-0.00	[1,2,3,4,5]

[a]- Factor to convert in mass basis 0.0024 kg of hydrogen per scf at 14.7 psi (1 atm) and 60 °F (15.6 °C).

[b]- Factor to convert in energy basis 3.59 MJ/kg of steam at 750 psi (5171 kPa) pressure and 1050 °F (565 °C) temperature.

[1] Gary, J.; Handwerk, G.; Kaiser, M., *Petroleum Refining Technology and Economics* Fifth ed.; CRC Press: New York, 2007.

[2] Maples, R., *Petroleum Refinery Process Economics.* Second ed.; PennWell Corp: 2000.

[3] Parkash, S., Refining Processes Handbook. Elsevier: Burlington, 2003.

[4] Skone, T.; Gerdes, K. *Development of Baseline Data and Analysis of Life Cycle Greenhouse Gas Emissions of Petroleum-Based Fuels* DOE/NETL-2009/1346; National Energy Technology Laboratory (NETL): November 26, 2008.

[5] Spath, P. L.; Mann, M. K. *Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming*; NREL/TP-570-27637; National Renewable Energy Laboratory: 2001.

PRELIM default values for process energy requirements are adopted from Gary et al. (2007). The data are described as "average, typical energy requirements" suitable for conducting economic analysis of different configurations close to the year of publication. As in the case of process unit yield correlations (section 5.3.3), the data applies for some refineries but not all. This reference is considered a good representation of basic performance indicators in industry based on discussions with industry experts (Karpe, 2009). However, users are encouraged to use their own data for these parameters in the `Constants` worksheet, if available. Table 4 details the default process energy requirements for each unit. The table aggregates the data to also include the range of energy requirements reported for the U.S. refining industry (Energetics, 2007) for comparison.

5.3.2 Hydrogen addition processes and global hydrogen mass balance method

One of the main functions of a refinery is to increase the hydrogen to carbon ratio of a crude through processing, and hence, convert it into more valuable products. Therefore, differences in hydrogen content between feedstock and refined products can be a significant factor that drives refinery GHG emissions. PRELIM uses a global hydrogen mass balance method to determine the hydrogen requirements for each hydroprocessing unit, taking into account the hydrogen produced by naphtha catalytic reformer and the differences in the feedstocks' hydrogen content. Some process units, such as the catalytic reformer and isomerization unit, are set to produce intermediate product streams with fixed hydrogen content. Contrastingly, all hydrotreaters are set to produce intermediate product streams with variable hydrogen content, which can be calculated by feed hydrogen content via linear regressions. Hydrocracker calculates the hydrogen content of intermediate products using correlations from Gary et al. (2007).

Hydrotreating and hydrocracking processes increase the hydrogen to carbon ratio of the feedstock by means of hydrogen addition. Hydrogen is added to the units at elevated temperature and pressure in the presence of a catalyst resulting in the removal of sulphur, nitrogen, and metals. Several chemical reactions occur and result in a hydrotreated liquid product and fuel gas (H_2S and hydrocarbon gas). The main distinction between hydrotreating and hydrocracking processes is the severity of conversion associated with their operating conditions. Hydrotreating occurs under milder operating conditions (lower pressure and temperature) as compared to hydrocracking. Therefore, in a hydrotreating process unit, the boiling range and hydrogen content of the process unit feed is only slightly altered. Conversely, the operating conditions in hydrocracking process units contribute to breaking the large hydrocarbon molecules of the process unit feed, increasing the yield of lighter products, and saturating aromatics and olefins (i.e., breaking the double or triple bonds between two carbon atoms present in these types of hydrocarbon molecules, and attaching the hydrogen to the carbon atom). Figure 3 shows the inputs and outputs as well as the subsequent process unit of the output for the naphtha, kerosene, diesel, and gas oil hydrotreating process units and for the gas oil and vacuum residue hydrocracking process units present in the model.

5.3.2.1 *Global hydrogen mass balance method at the process unit level*

In PRELIM, a global hydrogen mass balance method is used to determine hydrogen requirements in the hydrotreating and hydrocracking process units. Using this method, the hydrogen requirement for each process unit is calculated by taking the difference in hydrogen content between the mass of the process unit feed input (liquid feed) and the mass of the hydrotreated liquid product and fuel gas (Figure 7).
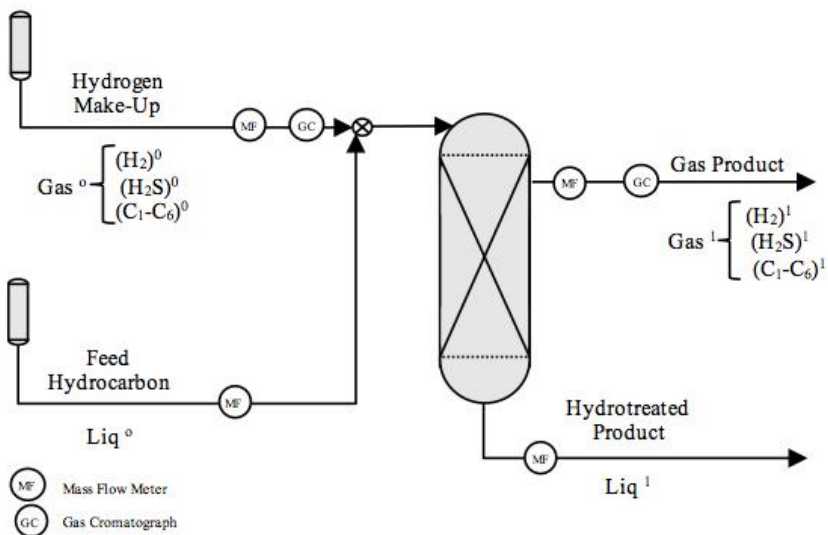
Figure 7: Global Hydrogen Mass Balance Method at the Process Unit Level

Figure modified from Castañeda et al. (2011)

This method is adopted because it accounts for the hydrogen content of each fraction and is a good representation of the hydrocarbon molecules present in any crude fraction. Also, it allows for a simple method to identify the destination of the hydrogen supplied (i.e., the hydrogen flow through the refinery and the identification of the source of the associated energy requirements and GHG emissions). Although the global hydrogen mass balance method is relatively simple, in PRELIM several additional assumptions are required and are outlined below.

5.3.2.2 Hydrotreating process unit assumptions

PRELIM estimates hydrotreater hydrogen use mainly based on the difference between input and output hydrogen content.

$$H_{consumed} = 1.05 * (H^1_{liquid} - H^0_{liquid} + H^1_{H_2S} + H^1_{NH_3} + H^1_{HCgas})$$

Previous versions of PRELIM set hydrotreater output hydrogen content as constants based on industry expert opinions, which may not reflect the actual variations of hydrogen caused by different types of refineries and different crude slates. Starting from PRELIM v1.4, thanks to proprietary industry datasets, these output hydrogen content values have been calibrated by proprietary industry data to be linearly associated with input hydrogen content rather than constants. In other words, for each hydrotreater, linear regression equations are obtained and adopted for all types of refineries (e.g., hydroskimming, medium FCC, deep FCC) to improve accuracy. Detailed steps are summarized as follows:

Step 1: For each type of hydrotreater in each refinery configuration, collect hydrogen consumption data ($H_{consumed}$) from corresponding refineries available from industry datasets. For example, for naphtha hydrotreater in the medium conversion FCC refineries, there are 81 consumption datapoints available from industry datasets.

Step 2: Run all selected refineries from Step 1 in PRELIM by using their transformed crude slates. Record hydrotreater inflow properties of the selected hydrotreater including $H\%^0_{liquid}$, sulfur content, and nitrogen content in wt.% for all selected refineries.

Step 3: Record H^0_{liquid}, $H^1_{H_2S}$, $H^1_{NH_3}$, and H^1_{HCgas} for all selected refineries.

Step 4: According to the above equation, calculate H^1_{liquid} and then $H\%^1_{liquid}$ for all selected refineries.

Step 5: Generate a linear regression equation based on the $H\%^0_{liquid}$ and $H\%^1_{liquid}$ of all selected refineries.

Step 6: Repeat Steps 1-5 for all other hydrotreaters and refinery configurations.

It should be noted that , as PRELIM does not distinguish between the structural compositions of the crude fractions (hydrogen content is an aggregated representation of the hydrocarbon molecules in the crude fraction), it is not feasible in the current version of PRELIM to track the quality of the final products to ensure they meet fuel specifications such as aromaticity. In real operations, if a crude with high aromaticity is processed in a configuration with milder operating conditions (i.e., lower pressure and temperature) rather than a hydrocracking process unit, the aromatics will remain unaffected and end up in diesel (Karpe, 2011). However, in hydrotreating process units, aromatics saturation is facilitated by operating variables such as hydrogen purity of recycled gas, pressure in products separator, type of catalyst, and ratio of volume feed to volume catalyst. These variables are related to the hydrogen partial pressure in the reactor. These variables are defined prior to the process unit operation by economic analysis and process unit design (Jones et al., 2006). PRELIM does not model these parameters and assumes that the hydrotreating units operate under the appropriate operating conditions to comply with the fuel specifications and that the hydrogen content of the final product represents the structural composition expected.

Another important assumption is the amount and quality of the fuel gas produced in the hydrotreating units define the process unit product yields by following a carbon/hydrogen mass balance method (i.e., hydrotreated liquid product and fuel gas). As the fuel gas produced in refineries is a mixture of streams generated in various refinery processes, its composition varies constantly. Usually, such fuel gas contains hydrogen, methane and ethane, some propane and butane, and higher molecular weight gases (Grover et al., 2007; Márquez-Riquelme et al., 2010). The ideal calculation to determine fuel gas production as well as its composition is refinery and unit operation specific: "Flash calculations for each unit operation (not each type of unit) to determine the offgas composition. There is no rule of thumb. Depending on design, the feedstock, and the severity, the hydrogen content could be anywhere from 10 to 60% of the combined offgases" (Karpe, 2010). Therefore, in PRELIM, the estimates of the mass yield and hydrogen content of fuel gas produced are a first approximation and will differ somewhat from real operations. The amount of fuel gas produced in hydrotreating process units is assumed to be composed of a hydrocarbon fuel gas free of sulphur (Figure 7, mass of H and (C1-C6) in stream Gas[1]) and hydrogen sulphide gas (Figure 7, H$_2$S in stream Gas[1]). The hydrocarbon fuel gas free of sulphur is assumed to be 0.2wt% of the process liquid feed (Parkash, 2003). Also, the hydrogen content of this fuel gas is assumed to be 17-21wt%, which represents a distribution of the hydrogen both in the hydrocarbons as well as the hydrogen present as H in the fuel gas (Grover et al., 2007). The mass of hydrogen sulphide (also known as acid gas) is calculated using the sulphur content of the liquid feed (i.e., sulphur content of the crude fraction), a percentage of sulphur removal through hydrodesulphurization (every mole of sulphur uses 2 moles of hydrogen to convert it into H2S). The hydrogen needed to produce the hydrogen sulphide is in addition to the hydrogen requirements from the fuel gas free of sulphur. The hydrogen consumption due to hydrodenitrogenation is accounted for by

including the hydrogen content of the liquid product in the calculation. Hydrogen consumption to remove nitrogen is negligible compared to the hydrogen needed to saturate the molecules from which this element is removed (see

Figure 9). These assumptions are needed to determine (by mass balance) the amount of liquid product coming out of the hydrotreating process units. The mass and volume yield estimates of liquid product from the hydrotreating process units neglect the slight change in the boiling point range of the hydrotreating process unit feed. The liquid product in real operations is separated into different intermediate products based on their boiling range (as crude is separated into its fractions). PRELIM assumes it to be a single product in the same boiling point range. Figure 8 explains these assumptions in more detail and illustrates the steps in the hydrogen mass balance for the hydrotreating process unit of the FCC feed (gas oil hydrotreating process unit). In addition, Figure 9 shows the calculated values for this combination of assumptions for a specific bitumen crude.

Hydrotreating of FCC Feed
Global Mass Balance:

$$Gas^0 + Liq^0 = Gas^1 + Liq^1$$

inlets (^{0}) and oulets (^{1})

Gas^0, Gas^1, and Liq^1 are unknown, then

Gas^1 Flow
Assumption
1. Yield of Fuel Gas [(C1-C6)+H2] ^{1}: 0.2 wt% of process liquid feed
$$\rightarrow Gas^1 = 0.002\ Liq^0 + H_2S$$

Liq^1 Flow
Assumptions
2. Hydrogen Make-up purity: 100%
$$Gas^0 = H^0$$
3. Fuel Gas Hydrogen Content [(C$_1$-C$_6$)+H2] ^{1} : 22 wt%
4. Hydrotreated Liquid Product (FCC Feed) Hydrogen content: 12.5 wt%
5. Hydrotreated Liquid Product Sulphur and Nitrogen content negligible
$\rightarrow Liq^1 = (Liq^0\ (1-\%H-\%S-\%N) - (Fuel\ Gas^1\ (1-0.22))/(1-0.125)$

Gas^0 Flow or Hydrogen Requirements
Global Balance of Hydrogen:
$$H^0_{Gas} + H^0_{Liquid} = H^1_{Gas} + H^1_{Liquid}$$

$H^0_{Liquid} = 0.22\ Liq^1$
$H^1_{Gas} = 0.22\ Gas^1 + H^1_{H_2S}$
$H^1_{Liquid} = 0.125\ Liq^1$

$$\rightarrow H^0_{Gas} = H^0_{Make-up} = Gas^0 = H^1_{Gas} + H^1_{Liquid} - H^0_{Liquid}$$

Figure 8: PRELIM Hydrogen Balance Calculation Method

Figure modified from Castañeda et al. (2011)

Global Mass Balance						
Gas Product (Gas¹)				FCC Feed Hydrotreater		

Global Mass Balance

Gas Product (Gas^1)

Fuel Gas yield [(C$_1$-C$_6$)+H$_2$]	0.2%	wt% Liquid Feed
Fuel Gas flow	15,273	kg/d
Desulfurization	99.9%	wt%
Sulfur in feed	408,751	Kg/day
Sulfur removed	408,342	Kg/day
H2S Gas flow	434,298	kg/d
Total Gas Flow (Gas^1)	449,571	kg/d

Hidrotreated Liquid ($_{LLiq}$^{1})

Fuel Gas Hydrogen Content [(C$_1$-C$_6$)+H$_2$]	22.2	wt%
Fuel Gas Carbon Flow [(C$_1$-C$_6$)+H$_2$]	11,883	kg/d
Hidrotreated Liquid Carbon Flow (C$_{Liq}$^{1})	6,375,864	kg/d
Total Hidrotreated Liquid Flow ($_{LLiq}$^{1})	7,286,701	kg/d

Hydrogen Balance

Liquid Feed Hydrogen Flow (H$_{Liq}$^{0})	816,352	kg/d	
Fuel Gas Hydrogen Flow [(C$_1$-C$_6$)+H$_2$]	3,391	kg/d	3% Hydrogen Requirements (H$_{Gas}$^{0})
H$_2$S Hydrogen Flow	25,547	kg/d	21% Hydrogen Requirements (H$_{Gas}$^{0})
Hidrotreated Liquid Hydrogen Flow (H$_{Liq}$^{1})	910,838	kg/d	
Hydrogen Requirements (H$_{Gas}$^{0})	123,423	kg/d	

Rationality Behind Neglecting Nitrogen

Denitrogenation (*Function of Process Hydrogen Pressure*)	99.9%	wt%	
Removed Nitrogen	23,832	Kg/day	
Hydrogen requirement for denitrogenation reaction	59	Nm3/m3/wt% change	
Hydrogen Consumed for denitrogenation reaction	13,227	kg/d	11% Hydrogen Requirements (H$_{Gas}$^{0})
NH$_3$ Gas Flow	5,107	kg/d	1% Total Gas Flow (Gas^1)
NH$_3$ Hydrogen Flow	901	Kg/day	1% Hydrogen Requirements (H$_{Gas}$^{0})
Hydrogen in Liquid Product due to Denitrogenation	12,326	Kg/day	10% Hydrogen Requirements (H$_{Gas}$^{0})

To Compare to Sulphur Removal

Removed Sulphur	408,751	Kg/day	
Hydrogen requiement for desulfurization reaction	25	Nm3/m3/wt% change	
Hydrogen Consumed for desulfurization reaction	96,036	kg/d	78% Hydrogen Requirements (H$_{Gas}$^{0})
H2S Gas flow	434,298	kg/d	97% Total Gas Flow (Gas^1)
H$_2$S Hydrogen Flow	25,547	kg/d	21% Hydrogen Requirements (H$_{Gas}$^{0})
Hydrogen in Liquid Product due to Desulfurization	70,489	kg/d	57% Hydrogen Requirements (H$_{Gas}$^{0})

To Compare to meet Hydriotreated Liquid Specifications

Additional Hydrogen to meet liquid product hydrogen specifica	828,023	kg/d	88% H$_{Gas}$^{0} + H$_{Liq}$^{0}

FCC Feed Hydrotreater

Property	Units	Total Feed to FCC HT Liquid 0	Hydrotreated FCC Feed	*Verification global and Hydrogen mass balance*
Vol Flow	bpd	50,273	50,365	
Vol Flow	m^3/d	7,993	8,007	
Mass Flow	kg/d	7,636,705	7,286,701	0.3%
Sulphur	wt%	5.4	0.0056	
Nitrogen	mass ppi	3,124	3	
API gravity	oAPI	16.60	23.99	
Density	kg/m^3	955	910.00	
Hydrogen	wt%	10.7	12.5	0.0%
Characterizatio Kw (Approximate)			11.8	

> In this example, the hydrogen balance is closed while the global mass balance has a deviation of 0.3wt% of the total mass amount of process liquid feed and hydrogen feed; the deviation mainly derives from neglecting the production of NH3 during nitrogen removal. In actual operations NH3 goes out with wash water (sour water) from the separator to th sour water stripper. From there it goes to the sulfur recovery unit along with H2S.

> In addition, PRELIM adds an input parameter of H loses as a wt% of the total refinery hydrogen requirement that represents "mechanical losses—"The hydrogen lost through the makeup and recycle gas compressors' packing vents and seals… roughly estimated at 3–5% of the combined chemical consumption plus solution losses"

> In general, the amount of hydrogen required for the chemical reactions associated to the removal of nitrogen has a minimum effect in calculation of hydrogen requirements once the hydrogen content of the liquid product is specified. Cross check of the hydrogen requirement estimates using stoichiometric molar ratios of hydrogen to hydrocarbon of the generic reactions (e.g 2 to 4 moles of hydrogen for mole of sulphur to convert it into H2S and saturate hydrocarbon where the S comes from with hydrogen) and hydrogen requirement estimates with average contributions of each of these two reactions to the hydrogen consumption (e.g., 100–150 scf H per each 1 of S wt% removed) validate the calculation.

Figure 9: Illustration of PRELIM hydrogen balance calculation for hydrotreating of fluid catalytic cracking feed

5.3.2.3 *Hydrocracking assumptions*

The level of conversion in hydrocracking processes and yields of process unit products depend on the type of catalyst and specific design of the process unit (Parkash, 2003). PRELIM hydrocracking product yields (mainly gasoline, medium and heavy gas oils, and fuel gas) are correlated to three parameters: 1) process unit feed API, 2) crude fraction characteristic boiling point, and 3) an approximated hydrogen requirement that can represent different levels of severity of the process unit operating conditions (i.e., the level of conversion sought). PRELIM uses correlations from Gary et al. (2007) that provide data for two feeds of extreme quality (paraffinic and highly naphthenic/aromatic) and three different levels of hydrogen requirements (500, 1500, and 2500 scf hydrogen/bbl). The correlations also provide a method to estimate the hydrogen content of the hydrocracking process unit products. The hydrogen requirements of the hydrocracking process unit are then calculated by the global hydrogen mass balance method. However, these correlations do not capture variation in process unit product yields due to changes in the type of catalyst, which varies among refineries.

5.3.2.4 *Origin of hydrogen supplies and greenhouse gas emissions associated with its production*

In PRELIM, the global hydrogen mass balance method is also applied to determine the yield of produced hydrogen and fuel gas from the naphtha catalytic reforming process unit. This process unit rearranges the carbon and hydrogen bonds of hydrocarbon molecules to increase the octane rating of naphtha fractions by dehydrogenation and production of aromatic components. In this case, the aromatic content of process unit feed and the yields of fuel gas and hydrogen due to process unit operating conditions are important matters. Hydrogen needed for hydroprocessing comes from two sources. One source is the naphtha catalytic reformer, the remaining comes from SMR where refinery energy use can be determined. In PRELIM, fuel gas is prioritized to be used first in supplying heat, second in steam production, and finally as a feedstock for hydrogen production (similar scheme to actual refinery operations). Natural gas is only used to offset energy requirements that are not supplied by the fuel gas and as the main feedstock for hydrogen production. The amount and energy content of the fuel gas

produced on site is subtracted from the total amount of energy required for all the refinery operations to estimate the amount of natural gas that is required from offsite, along with its upstream GHG emissions. Also, the amount of hydrogen produced from the SMR is one of the main contributors (up to 1/3 to 1/2) to the GHG emissions from a refinery. The emissions are mainly CO_2 that is produced during the chemical transformation of natural gas into hydrogen (chemical reaction in which a mole of CO_2 is formed for every mole of carbon in the natural gas), in addition to the combustion emissions from supplied fuel and steam used to satisfy the SMR process energy requirements. Using PRELIM default values, direct refinery emissions from either using natural gas or refinery fuel gas are similar as it is assumed that the hydrogen content of both feedstocks are similar. However, natural gas does carry additional upstream indirect emissions, which can result in higher refinery emissions when RFG is not assumed to be consumed onsite. Preliminary results also show that the heating value, the amount of refinery fuel gas and the range of possible emissions factors for the refinery fuel gas does not have a significant effect on the refinery GHG emissions (see sections 5.2 and 5.3.1 from Abella [2012] for details).

Hydrogen balance is the most challenging task in modelling refinery operations. In real-world contexts, the hydrogen balance of a refinery can be affected by a lack of accuracy in the measurement of flow rate and hydrogen content of refinery streams (e.g., purge gas from a high-pressure hydrocracker) (Stratiev et al., 2009). At the process unit level, the most common method used by refinery operators – based on the hydrogen balance of the gas streams (streams Gas^0 and Gas^1 in Figure 7) can underestimate hydrogen consumption up to 6% (Castañeda et al., 2011). When the process unit streams (e.g., liquid feed, hydrotreated liquid product, and fuel gas) are experimentally characterized, the global hydrogen mass balance method is considered more accurate than simple calculation methods used by refinery operators (e.g., based on the type of crude fraction processed and process unit volume feed or based on the hydrogen balance of the gas streams). When the global hydrogen mass balance method is adopted based on empirical correlations, the hydrogen requirement estimates can have a standard deviation that ranges from 9 to 15% compared with experimental data for hydrotreating processes (Castañeda et al., 2011). Several other methods exist to determine the hydrogen requirements of hydrotreating processes (see for example Castaneda et al. [2011] and Stratiev et al., [2009] for a description and comparison of such methods). However, they require a high level of complexity in modelling (more detailed representation of the chemical reactions that take place) that is not desirable for the purposes of policy analysis or additional data inputs. Also, they do not perform better than a global hydrogen mass balance based on empirical correlations. Deviations from experimental data for all methods are specific to the type of crude fraction hydrotreated, but standard deviations can be as high as 50% (Castañeda et al., 2011). The PRELIM global mass hydrogen balance approach (i.e., the use of approximations for hydrogen content instead of empirical correlations associated with the structural composition of the molecules) is also evaluated against a more detailed and different modelling approach for validation purposes (sections 7.1 shows the methods and 8.4 shows the results).

5.3.2.5   Surplus Hydrogen

Some crudes have more hydrogen in certain fractions than what is needed to meet the specifications of the intermediate or final products. In a refinery, such situation would be dealt with by blending crudes in such a way to meet specifications with minimal amounts of additional hydrogen required. Since PRELIM can estimate energy and GHG emissions for an individual crude, this needs to be handled in a slightly different way. This surplus can occur in hydrotreaters throughout a refinery or in naphtha catalytic reformer (NCR). The type of surplus is different for these two types of units. That is, hydrotreater hydrogen surplus is simply a higher hydrogen content of liquid hydrocarbons. Therefore, despite exceeding the specification needs, this type of hydrogen is not readily available to be extracted and used in other refinery process units; instead, the streams exiting hydrotreaters simply contain

hydrogen content that are higher than the intermediate product specifications. This is different for the surplus hydrogen generated from NCR. This hydrogen is in its gaseous form that can be readily used by a variety of other process units. Therefore, the amount of hydrogen produced by NCR is prioritized to be used for satisfying hydrogen requirements in the refinery. If the amount of hydrogen from NCR is not enough to meet the total refinery demand, SMR will be used to supply the remaining amount of hydrogen. If the amount of hydrogen from NCR is more than the demand, then SMR will not be used. Again, in a refinery this would be used to process other crudes in the refinery. To calculate the energy and GHG emissions associated with a crude that produces a surplus of hydrogen, this must be considered. This can be done in several ways. Below we describe the simple way in which PRELIM handles this surplus for the two main functional units currently available in PRELIM.

5.3.2.5.1 Total refinery emissions and crude emissions intensity for surplus hydrogen cases

For results displayed using the functional unit of per bbl of crude input, any surplus hydrogen produced in the NCR is considered a product as it still consumes utilities. Ultimately, this hydrogen could be used to process other crudes or sold outside of the refinery. It is possible to consider a credit for this hydrogen if it offsets another product (e.g., SMR produced hydrogen), however, what is being offset must be determined in order to do this. Therefore, the total refinery emissions will include the emissions associated with producing this product, and PRELIM reports the amount of surplus hydrogen that is produced within the product slate output tabs. If surplus hydrogen occurs in the hydrotreaters, the hydrogen is simply carried into the output product stream. The value of this additional hydrogen is uncertain. A future version of PRELIM could explore ways to credit this surplus.

5.3.2.5.2 Impact on emissions per final product

For results displayed using the functional unit of per MJ of final product, any surplus hydrogen produced by NCR is considered a final product and have emissions allocated to it. This results in a reduction of emissions for the rest of the product slate. To date, any crude that produces surplus hydrogen has altered product emissions by negligible amounts. In addition, if a high-quality crude is being run in the model and the hydrogen content in the input stream to a hydrotreater is higher than the output hydrogen content assumption for that hydrotreater, the hydrogen requirement would be only that to remove sulphur.

5.3.3 Carbon rejection processes and product yields

FCC and delayed coking can both increase the hydrogen to carbon ratio of the feedstock by means of carbon rejection. Heavy material is broken into molecules with a variety of hydrogen to carbon ratios under certain pressure and temperature conditions. The vapours of those molecules with the lowest hydrogen to carbon ratio condense to form produce coke ("large polynuclear aromatics precipitate to form crystalline liquids and ultimately solidify to form coke", Robinson [2006]); the remaining material is separated into desired process unit products by fractionation. Figure 3 shows the inputs and outputs as well as the destination of the outputs for FCC and delayed coking process units in the model.

5.3.3.1 Fluid Catalytic Cracking process unit

The FCC process upgrades crude gas oil or medium fractions (atmospheric and vacuum gas oils) in the presence of a powdered catalyst whereby coke formation is minimized during the cracking of the heavy hydrocarbons. During its operation, coke is formed and deposited on the surface of catalyst, which needs to be recovered and regenerated by burning off the unwanted coke (i.e., catalyst regeneration process). Energy recovered from the combustion of coke supplies heat to both cracking reactions and vaporizing the FCC feed (Parkash, 2003). In

addition, gases from coke combustion possess energy content that can be recovered for use in the process unit (e.g., production of electricity using a turbo expander or steam generation using a waste heat boiler).

In PRELIM, FCC product yields (mainly gasoline, medium and heavy gas oils, unsaturated LPG, fuel gas, and coke) are correlated to two parameters: 1) conversion of process unit feed into different products (PRELIM input parameter) represented by process unit operating conditions (i.e., temperature, pressure, and catalyst to oil ratio), and 2) a characterization parameter called Watson characterization factor (Kw) that can represent the structural composition of a crude fraction based on the characteristic boiling point and specific gravity of the fraction (Watson, 1933). Highly paraffinic crudes will have a Kw greater than 12 while highly naphthenic or aromatic materials will approach 10 as a minimum value (Watson, 1933). The structural composition is a key feed characteristic for the operation of FCC. Aromatics crack less easily than paraffins. Therefore, high aromatic content in the FCC feed can increase the yields of coke and fuel gas and thereby decrease the yield of gasoline and the overall conversion efficiency (Parkash, 2003). Based on Gary et al., 2007, PRELIM by default assumes the use of a zeolite catalyst in FCC and adopts two benchmark Kw values (11.8 and 12.4) for calculations. If the Kw of FCC feed is less than the midpoint (i.e., 12.1) of these two benchmarks, then 11.8 will be used to replace the actual feed Kw. Although being efficient and simple to implement, such assumptions cannot accommodate variations in FCC yields due to changes in the type of catalyst that varies among refineries or due to the use of highly naphthenic/aromatic feeds (very low Kw). In addition, PRELIM also includes an alternative calculation method that assumes a constant distribution of products yield if specific yields are known by the user.

Starting from PRELIM v1.4, FCC post hydrotreater is the default option for FCC hydrotreating (i.e., the `Fluid Catalytic Cracking options` dropdown menu in the `Main Input & Output` worksheet). FCC Feed Hydrotreater (83 out of 363 refineries worldwide according to the proprietary industry dataset) is not as widely deployed as FCCPHT (216 out of 363 refineries worldwide) because it may not be economically worthwhile to treat all incoming FCC feed, unless more high quality gasoline is desired from FCC than diesel.

User can still manually override FCC hydrotreating option by selecting FCC feed hydrotreater (i.e., default option in PRELIM v1.0-1.3, which usually leads to higher hydrogen consumption for FCC hydrotreating. For example, PRELIM allows the FCC unit to upgrade coker gas oil products from delayed coking. Coker gas oil may be highly naphthenic/aromatic (based on the quality of the crude), hence the expected Kw can be lower than 11.8 (e.g., Fisher [1990] presents Kw values for different FCC feedstocks that range from 10.7 from a fluid coking-derived vacuum gas oil to 11.5 for a Canadian conventional crude). Hydrotreating such FCC feed saturates some of the hydrocarbon molecules present, decreasing the relative amounts of aromatics and naphthenes in the gas oil fractions to be represented for a high Kw value. It is assumed that the Kw curve of 11.8 applies in such cases. Additionally, a conversion of 75% is used as a default value as it is recommended to be used for heavy crude fractions by Gary et al. (2007).

There is uncertainty associated with the product yields resulting from the FCC unit. PRELIM v1.1 shows that the Kw factor calculated for the blend of gas oil fractions (i.e., AGO, HVGO, and LVGO) of the crudes included in PRELIM crude assay inventory (without including delayed coking gas oils and hydrotreating) ranges from 10.88 to 12.87. Starting from PRELIM v1.2 and onwards, a Kw factor of 11.5 (as opposed to Kw factor of 12 in PRELIM v1.1) is assumed for the delayed coking gas oil product, the range narrows down to 11.38 to 12.44. PRELIM by default assumes that FCC feed is hydrotreated only enough to achieve either Kw factor. Highly naphthenic/aromatic gas oils are assumed to change their Kw from 11.38 to 11.8 while paraffinic crudes are assumed to essentially sustain their Kw at 12.5. In this case the FCC product yields can be considered appropriate. On the other hand, when the fluid catalytic cracking feed hydrotreater is disabled (FCC gasoline is hydrotreated instead), any FCC feed with Kw

below 11.8 will remain unchanged, and the FCC product yields can be expected to deviate from the estimates using feed hydrotreater and the Kw 11.8 curve. The impact of this modelling characteristic is crude specific.

5.3.3.2 Delayed coking

Delayed coking can upgrade a variety of feedstocks, typically including the heaviest fraction resulting from the vacuum distillation process (i.e., vacuum residue). The delayed coking process occurs in the absence of any catalyst and the conversion of residue into lighter products occurs by means of heat alone; high residence time favours the cracking reactions and the amount of coke produced is considerable (e.g., for the current assay inventory, coke yield can be up to 40%wt of a crude vacuum residue fraction). Variation in operating conditions such as temperature and pressure, in addition to process unit feed quality, can affect the amount of coke produced as a refinery final product.

In PRELIM, the delayed coking process unit product yields (i.e., coke, fuel gas, coking heavy naphtha, and [indirectly by means of mass balance] coking gas oil yields) are linearly correlated to the amount of carbon residue in the process unit feed (Gary et al., 2007). "The carbon residue is the residue that remains after evaporation and pyrolysis of crude oil under given conditions..., it is indicative of the coke-forming tendency of the crude under thermal degradation conditions" (Hassan et al., 2009). The use of such correlations is important because it accounts for the quality of the heaviest fractions of the crude and uses a parameter that is easy to measure. For example, a technique such as Micro Carbon Residuum (MCR) uses small amounts of sample and simple laboratory instruments (Hassan et al., 2009). PRELIM uses correlations from Gary et al. (2007) for coke and liquid yields based solely on carbon residue. However, in the delayed coking process unit, temperature, pressure, and product recycling ratio are used to control delayed coking yields and product quality (Parkash, 2003). By using the Gary correlation, PRELIM will not capture variations in delayed coking product yields due to changes in these operating conditions.

5.3.4 Alternative value-added processes

5.3.4.1 Refinery Fuel Gas Upgrading: Liquefied petroleum gases and petrochemicals

Liquefied Petroleum Gas (LPG) and petrochemical feedstocks are refinery products produced by the light ends of the crude. These are valuable products which are commonly produced from refineries in smaller quantities than transportation fuel products.

PRELIM v.1.0 assumed that propane and butane, derived from different process units, are used as a refinery fuel gas and blended into gasoline respectively. However, this represents only one possible destination for these intermediate products. Refineries can opt for recovering the propane and butane to be sold as petrochemical feedstock or as a combination of gases to be sold as LPG. Some refineries consider gasoline as a more economically desirable product than LPG and blend most butanes into gasoline, as n- butane or as alkylate after being isomerized (isobutene) and transformed in an alkylation process unit (Gary et al., 2007).

Starting from PRELIM v.1.1 and onwards, a calculation method is adopted to differentiate lighter gases derived from the refinery's various off-gas streams produced on site and allows for considering a scenario where LPG and/or petrochemicals are produced. Traditional refining linear programming modeling approach and current PRELIM life cycle system level approach are described in the following two sections:

5.3.4.1.1 Modelling detail to differentiate refinery crude feedstock impacts

To model the alternative production pathways of LPG and/or petrochemicals in a way that reflects changes in refinery crude feedstock, detailed modeling and data are needed. It requires light ends crude assay data (volume percent distribution of the low molecular weight compounds that are present in the crude and include, but are not limited to, methane, ethane, propane, and butanes), and an estimate of the mass fraction of these components for each crude assigning/using molecular weight and density to each component (i.e., pseudo-components method [Parkash, 2003]). In addition, it is necessary to include a material balance component that allows for tracking the different sources of propane and butane through the model. For example, PRELIM model routes C3 and light ends in the hydrocracking process unit to the refinery fuel gas and the C4 to gasoline, while it sent the C3 and C4 in the FCC process unit to the alkylation process unit. Finally, a light ends recovery plant was added to PRELIM. It is mostly distillation process units that separate these gases in the same way that the crude is separated into its fractions.

These modelling components could be incorporated into PRELIM structure for the purposes of modeling LPG and/or petrochemicals as a final product. However, the level of complexity associated with modelling LPG and/or petrochemicals production will not necessarily result in a better differentiation of the refinery energy use and GHG emissions associated with a crude. A rough estimate, based on runs of a proprietary model, indicated that less than 5%wt of the whole crude can end in a light ends recovery plant, and less than 2wt% of the whole crude can be transformed into LPG in a refinery with similar structure as represented in PRELIM (Baker & O'Brien). Basically, overall refinery energy use and GHG emissions would be affected by the energy use linked directly to processing this amount of material in the light ends recovery plant. However, refinery products energy and GHG emissions intensity will vary depending on the process-based allocation method used to assign these to each crude. Having said this, direct separation of LPG from light naphtha (light straight run) is expected to be added in future versions of PRELIM.

5.3.4.1.2 Modelling LPG and Petrochemicals as final products and default specifications

To model LPG and/or petrochemicals production, PRELIM includes a calculation method to differentiate lighter gases derived from the crude distillation process unit or from fuel gas produced on site. The method includes four major assumptions:

1. All LPG and petrochemical feedstocks are contained in the off-gas streams (otherwise used for refinery fuel gas (RFG)) produced in various process units;
2. The breakdown of molecules within the off-gas streams at each process unit is constant;
3. Final products are defined by the amount of type of molecules estimated after accounting for crude specific process unit flow feed and constant off gases composition;
4. All ethane, ethylene, propylene, and butylenes gases contained in the off-gas streams are recovered as the petrochemical feedstocks; Petrochemical feedstocks are highly valuable - $805/metric ton global average in 2015 (Platts, 2015), and their production would likely be preferred relative to RFG and LPG production from light ends;
5. All propane and butane gases are recovered as LPG (excluding butane recovered as intermediate product from gas oil hydrocracking and FCC and sent to gasoline); and
6. If LPG and/or petrochemical feedstocks are produced, then other gases (mainly methane) remain as RFG to be used within the refinery as fuel or produced as a product; if not, all off-gas streams are treated as RFG that can be used onsite or produced as a product.

This is a simplification over the detailed modelling required to differentiate crude oils based on extensive crude assay information and calculation methods that trace each type of molecule through each process unit and configuration. It can only reflect limited changes in refinery energy and emissions due to changes in crude feedstock (i.e., it captures only changes in distillation curves) and does not reflect changes on process unit operating conditions. However, this method is intended to capture changes in products' energy and emission intensities because of configurations (See section 0).

The off-gas streams' compositions at each process unit are assumed based on various literature sources including Gary & Handwerk, 2001; Baukal, 2013. Each process unit off-gas compositions is assumed below:

Table 6: Molecular breakdown of RFG from Various Process Units

	Mass %												
	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8	iC_4	nC_4	C_5+	H_2	N_2	H_2S	Total
Density(kg/m^3) at 20C, 1atm	0.67	1.20	1.26	1.75	1.88	2.50	2.51	2.50	3.23	0.08	1.17	1.43	
Reformer	14.7	6.61	27.8	4.12	32.6		13.8			0.33			100.00
Isom					13.1		52.3	34.7					100.00
NHT	5.22		9.88		27.2		21.8	31.7				4.23	100.00
KHT	5.03		5.03		18.1		37.8	19.4				14.6	100.00
GO-HC	44.6	3.70	20.8	3.59	13.5	2.57	7.73		3.31	0.26			100.00
DHT	5.03		5.03		18.1		37.8	19.4				14.6	100.00
Coker	22.0	2.96	21.8	1.44	37.1		14.4			0.28			100.00
CNHT	5.22		9.88		27.2		21.8	31.7				4.23	100.00
FCC FHT	3.25		6.16		11.6		24.3	12.5				42.2	100.00
FCC	17.4	6.82	9.24	21.30	38.2					0.41	6.63		100.00

Within PRELIM, the above numbers have been normalized to account only for the species present in the carbon-rich stream, i.e. CH_4 to C_5+.

5.3.4.2 Heavy End Upgrading: Asphalt

5.3.4.2.1 Modelling detail to differentiate refinery crude feedstock impacts

Asphalt is a non-combustible product produced from the heaviest ends of a crude oil. To model the alternative production pathway of asphalt that reflects changes in refinery crude feedstock, experimental and specialized crude assay data is needed. For example, correlations have been developed to estimate asphaltene content of heavy ends based on properties such as refractive index and specific gravity (Riazi, 2005). However, Saturate, Aromatic, Resin, and Asphaltenic (SARA) constituents of asphalts can vary between crudes and specifications (Corbett, 1969) and are not typically available in crude assays.

5.3.4.2.2 Modelling Asphalt as final products and default specifications

PRELIM uses a simplified approach based on typical refinery production information. Data from the U.S. Refining Survey 2015 (OGJ, 2014) showed that the vacuum distillation unit (VDU) capacity has a better correlation with daily asphalt production than any other parameters tested (e.g., atmospheric column capacity, fluid coking capacity, delayed coking capacity, and refinery Nelson Complexity index).
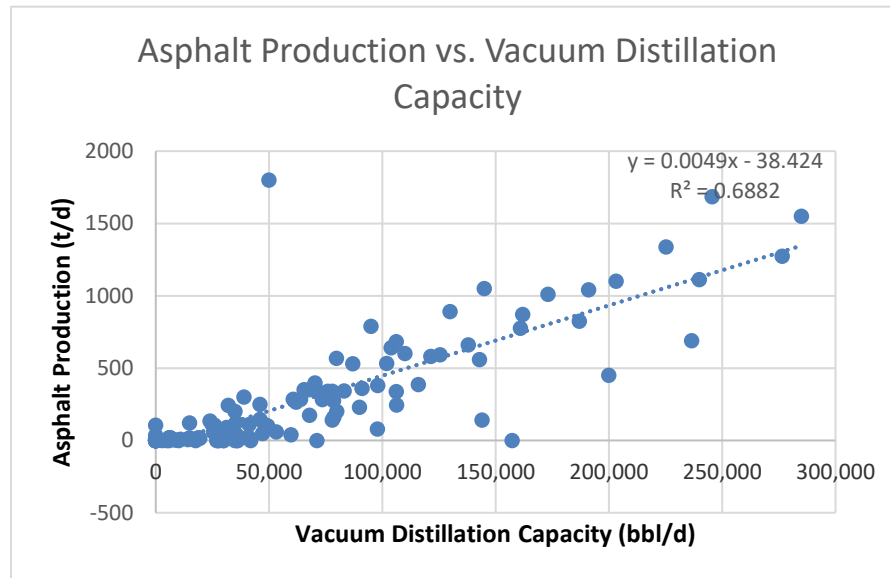
Figure 10: Asphalt Production versus vacuum distillation unit capacity

PRELIM uses the above correlation as an initial indicator of asphalt production. The correlation is used to determine a default asphalt production value that the user can select within PRELIM in the `Main Input & Output` worksheet. The use of the correlation is constrained by a maximum value of production. Based on expert input, a maximum value of 15% of the vacuum distillation capacity is allowed, to account for the variance possible for asphalt production. In the case where 15% of the vacuum distillation capacity is greater than the total vacuum residue of specific crude, then a new constraint is set up, and 99% of the vacuum residue is set as the maximum asphalt production. If the `asphalt configuration` is enabled, the maximum value is increased to 75% of the vacuum distillation capacity, as opposed to 15%.

5.3.5 Cogeneration Unit

Starting from PRELIM v.1.2 and onwards, calculations for cogeneration are added to both `RefineryCalcs` worksheets. Cogeneration of heat and power (CHP) technologies offer a more efficient way of supplying heat and electricity with less emissions in comparison to the commonly used separate heat and power units. CHP technologies can be applied to industrial processes, specifically in refineries. The following is a brief description of each of the technologies modelled in PRELIM (a more detailed description can be found in the EPA's Catalog of CHP Technologies [2015]):

1. Gas Turbine: One of the mostly used technologies, it consists of a compressor, a combustion chamber and an expansion turbine that runs on the Brayton thermodynamic cycle. Essentially, fuel is combusted to heat air that is used to drive the expansion turbine and generate electricity. The waste heat from this process can be used in other industrial applications, such as producing steam.
2. Microturbine: A smaller and a mechanically simpler version of a gas turbine. Not capable of producing high pressure steam.
3. Reciprocating Engine: Another widely used technology with two primary designs, the Otto-cycle and the Diesel-cycle. Mechanically, they are both the same where fuel is combusted to linearly drive a piston,

which in turn rotates a crankshaft that generates power. Again, heat can be recovered to use in other processes. Like the microturbine, this technology is not capable of producing high pressure steam.

4. Steam Turbine: This technology, unlike the previous ones, produces electricity as a by-product of generating steam. Operating with the Rankine cycle, water is heated to medium to high pressure steam, which is expanded to drive a turbine that generates electricity. Once the steam has passed through, it is then used in other processes.

5. Fuel Cell: This technology operates like a battery, but unlike a battery, has a continuous fuel source. It consists of a cathode, an anode, an electrolyte and an external load. A fuel processor converts the fuel into a hydrogen rich stream and fed into the fuel cell along with oxygen. The hydrogen and oxygen react at the anode and cathode, respectively, generating a direct current. Heat is produced as a result of this reaction, which can be used in other processes.

6. Natural gas combined cycle (NGCC): This is a combination of steam and gas turbines.

It is assumed that all CHP technologies satisfy utility demands at a process unit level. Thus, to calculate the refinery energy requirements with cogeneration, PRELIM compares the refinery's base electricity requirement for each process unit to the activated cogeneration technology's nominal capacity. The conditions of the modeling are pre-set such that only the onsite demand for electricity is satisfied and no excess exportable electricity is produced. Given CHP aims at satisfying electricity needs first, if the heat produced by the CHP technologies is not enough to meet the heat required by the refinery, then natural gas is assumed to be used in the refinery's boilers and furnaces to provide additional heat to meet these requirements (Note that the heat produced by the CHP system is first used for steam production. Any additional heat from the CHP system will then be used towards satisfying the heat requirement of the refinery). The steam produced by the CHP steam would otherwise have to be produced in the refinery boilers that consume natural gas, and electricity. For the steam turbine CHP system, the total steam requirement of the refinery was assumed to be satisfied by this technology, and the electricity produced by this technology was supplemented by electricity from the neighboring power grid. The modelling parameters used for the CHP technologies are all from the EPA's Catalog of CHP Technologies [2015] and these values are summarized in the `Constants` worksheet. It is assumed that the CHP operates at the maximum power-to-heat ratio.

The amount of fuel required for the CHP technologies was calculated using the following equation (Motazedi et. al, 2016):

F=(P+H)/η

Where:

F is the total fuel requirement for the CHP system (MW)

P is the net power output of the CHP system (MW)

H is the net heat output of the CHP system (MW)

η is the total efficiency of the CHP system

The fuel consumed by the CHP system is added to the total heat requirement for each process unit. Note that the CHP efficiency used in PRELIM is taken as the average between the maximum and minimum efficiencies. PRELIM does not currently consider any excess electricity to be exported to the grid.

5.4 Controls – Advanced features

The `CokingRefineryControls` and `HydroRefineryControls` worksheets are where PRELIM offers users with flexibility to modify volumetric flow rates among key process units in order to fine tune a refinery configuration or to better match a desired product slate. Basically, the objective of these worksheets is to gather PRELIM swings modelling information for further calculations and/or use of modelling tools (e.g. macros or solvers). Swings are flow splitters that distribute flows between process units.

> It is recommended that these worksheets should only be modified by experienced users as such operation may result in the model becoming unstable.

5.4.1 Product Slate Optimization

In PRELIM, by default, flow volumes and masses from the distillation columns are determined by the selected crude oil assay (i.e., different cuts such as LSR, naphtha, and diesel). These flows are then directed to and distributed among the proceeding process units using the swings or flow splitters. The swings have a set of default splitting ratios to either model a refinery configuration (e.g., minimizing flow to enable process units) or to allow product slate optimization by which the default values of flow volumes can be revised by experts or experienced users.

Although PRELIM is not intended to model individual refineries, to allow some flexibility in adjusting the abovementioned swings, three calculation procedures are set up in PRELIM that would allow the use of flow redirection to obtain (1) a specific gasoline share in product slate, (2) a specific gasoline to diesel ratio in product slate, and (3) a specific product slate. The basis for these procedures is performing trial and error procedures by varying the swings settings. This requires the installation and use of Excel solver.

The goals of product slate optimization procedures (e.g. maximizing gasoline production) are defined by setting up different constraints for the solver. After the desired final target of each optimization procedure is set, the solver automatically runs by changing the swing settings to produce results as close as possible to the target.

The first units where splitting/mixing of flows can occur are the distillation columns (atmospheric and vacuum towers). The model can mix the streams coming out of the column. Each of these streams can be mixed with heavier or lighter streams adjacent to them. Then, splitting/mixing occurs among connected process units. Currently the splitter has the following assumptions:

- Mixing of distillation column streams is limited to be lower than 10 vol. % of each stream.
- Mixing at other swings can occur with no restriction in the split of their input stream in any proportion between their output streams.

Using the first two optimization procedures is straightforward, and they can be run by only specifying the desired gasoline production value or the desired gasoline to diesel ratio at the `Expert Input` worksheet. Using the third optimization feature requires manually specifying the desired share of each product in product slate via the `Expert Input` worksheet.

The first tool requires specifying the percentage of gasoline in product slate such that the optimization procedure can vary the shares of other products freely in order to get as close as possible to the specified amount of gasoline. The second optimization procedure requires a specific gasoline to diesel ratio as input and can also freely change the shares of other products in order to yield the desired gasoline to diesel ratio. The specification of the gasoline

to diesel ratio sets constraints on both gasoline and diesel production, indicating slightly constrained solver search domain and therefore slightly less flexibility compared to the first optimization procedure.

For the third optimization procedure, the whole product slate needs to be specified. Solver calculations in this case are much less likely to converge to the exact specified product slate due to the large number of constraints that need to be satisfied. This procedure only tries to get as close as possible to the desired product slate, especially if the desired product slate is significantly different from the original product slate obtained from PRELIM default settings (without optimization).

5.4.1.1 Diesel/Jet Fuel Swing

PRELIM uses information on crude fraction yields at nine cut temperatures to determine flows from distillation columns (see details in section 5.5.3.1). Such temperature cutting scheme is not unique, and in real-world operations the boiling temperature ranges of each crude fraction can vary based on desired refinery product slates (Gary et al., 2007).

A comparison of PRELIM product slates to US PADD l product slate production levels shows that overall, PRELIM v1.0 predicted higher amounts of diesel and lower levels of jet fuel. Figure 11 shows all PRELIM crudes between the API range of 26 and 35, operating in a medium conversion refinery. The annual PADD level production from 2014 is also shown for comparison.
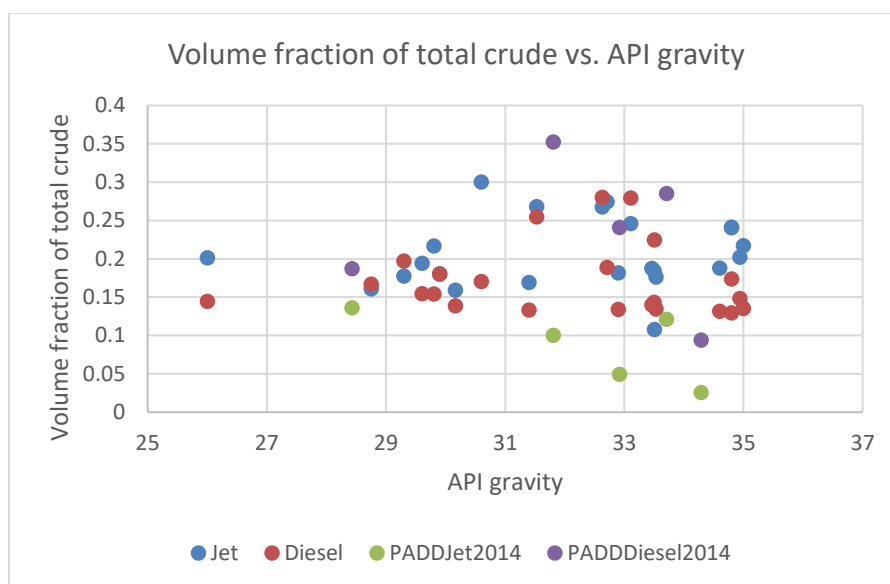
Figure 11: Comparison of PRELIM product slate to US net production (medium conversion)

Similarly, the same graph is plotted for a deep conversion FCC coking refinery for comparison:

Volume fraction of total crude vs. API gravity
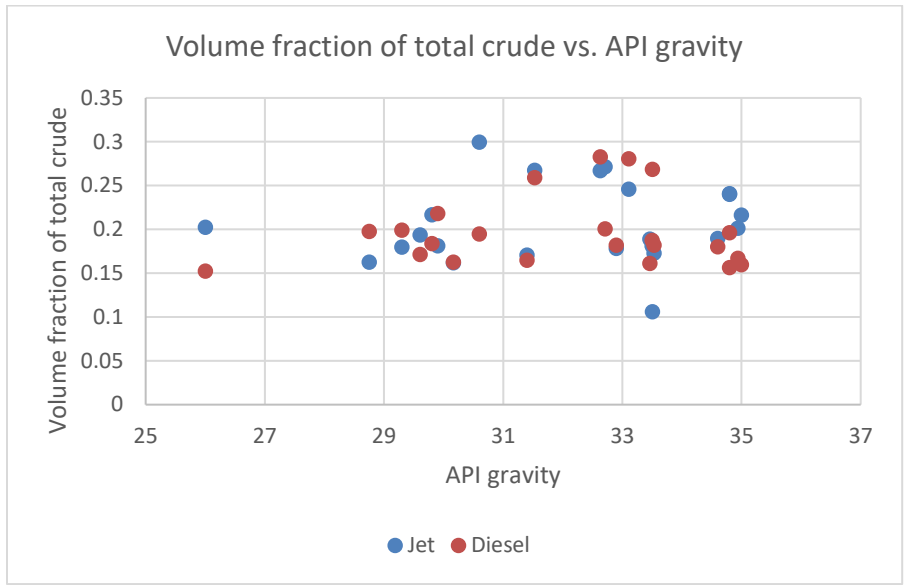
Figure 12: Comparison of PRELIM product slate to US net production (deep conversion)

As seen in Figure 11 and Figure 12, changing from a medium to deep conversion configuration has no effect on jet and diesel production, and does not explain the larger production of jet fuel over diesel fuel.

To model a refinery scenario closer to overall U.S. refining operations, PRELIM v1.1 incorporates an option to alter PRELIM default crude cutting scheme and model a refinery operation where diesel production is maximized over jet fuel/kerosene production.

First, the magnitude of the potential variation in the cutting scheme was evaluated comparing PRELIM estimated values for transportation products slate and jet fuel production to diesel production ratios to actual U.S. PADD 2014 reported data. Representative crudes, which have the closest API values to average API values for refined crude in 2014, were chosen for each U.S. PADD, and were run through PRELIM medium conversion coking and FCC refinery configuration as the basis for comparison.

Figure 13 shows that, for the representative crudes, PRELIM estimates different transportation fuel ratios. Notably, jet fuel production is usually higher, and diesel production is usually lower.

The amount of jet fuel/kerosene swing cut required to match the jet-diesel ratio was calculated for each PADD (see Table 7).

Table 7: Swing needed for PRELIM product slate to resemble 2014 PADD net production

PADD	Diesel-Jet Ratio (2014)	Representative Crude 1	Swing Needed (volume fraction whole crude)	Representative Crude 2	Swing Needed (volume fraction whole crude)
1	3.694	Canada Hibernia_Exxon	0.120	Azeri Light_Statoil	0.152
2	4.898	Thunderhorse_Exxon	0.128	Bonny Light_Chevron	0.157
3	3.520	AlaskanNorth Slope_Exxon	0.102	Nigera Bonga_Exxon	0.152
4	2.352	Thunderhorse_BP	0.090	North Sea Dansk Blend_Statoil	0.086
5	1.373	MarsUSA-Gulf of Mexico_BP	0.023	Brazil Lula_BG Group	0.020

Finally, to reflect a scenario of current U.S. petroleum refinery product slate for these distillate products, the user inputs `Jet-Diesel Swing` for the coking and hydro refinery modelling structures were added in PRELIM v.1.1 and onwards in the `Expert input` worksheet. The inputs `Jet-Diesel Swing` allows a change in the fraction volume of jet fuel/kerosene crude cut that can be directed to diesel production. For example, Table 7 above shows the amount of jet-diesel swing that could be required for the specific crudes to represent production rations in a PADD. Based on expert input a constraint has been included in the model to limit the jet fuel/diesel swing to 10% (volume of kerosene). This type of swing would certainly satisfy flash point specifications, using Semenov's proposed equation for flash point of petroleum fuel blends (Semenov, 1984), which allow a fuel blend of 70% jet, 30% diesel to meet a flash point spec of 55°C. In practice, the limiting specifications of mixing jet fuel into diesel are cetane number and viscosity (de Klerk, 2012) and they are not currently modelled in PRELIM. In addition, this constraint accounts for the fact that swings at the distillation process can be obtained by different operation modes to a maximum of variation of 20 Fahrenheit degrees in the true boiling point cut temperatures for which the process was designed. Although a large variation in jet fuel/kerosene yields may be possible; those are defined at the design phase of the refinery when the crude cut temperatures are selected. The assessment of PRELIM cuts compared to U.S. PADD refinery yields indicates that PRELIM has a large yield in Kerosene default cut temperatures, and any potential variation to represent North America refineries can be accounted for by using the `Jet-Diesel Swing` option.

> Notice that use of this option applies for the assessment of the refinery at a systems level. However, it does not allow a consistent comparison among crudes as any percentage change in volume flow of the jet fuel/kerosene fraction does not represent a similar and consistent change in the crude oil boiling temperature range among all crudes. The consistent comparison of crudes is allowed by the use of assay information at standard cut temperatures for all crudes.

5.5 Calculations external to PRELIM - PRELIM crude assay inventory

The PRELIM Crude Assay Inventory is developed to allow the user to select from a predetermined list of crude assays. If the user does not have access to their own assay, they can select a proxy crude that is close to the one they are interested in investigating without having to collect or measure additional data. However, any petroleum-based crude assay can be transformed and run in PRELIM. The construction of the assay inventory requires transformations of simplified data in the public realm and demonstrates a method that can be used by others. The current PRELIM v1.4 crude assay inventory includes **144** publicly available crude assays from different fields in various countries obtained from the websites of different major oil companies (BP, Chevron, ExxonMobil, and Statoil) as well as from the Knovel database and the Canadian Crude Quality Monitoring Program (CCQMP, http://www.crudemonitor.ca), with permission from these sources. The inventory thus includes a comprehensive range and diversity of crude quality. Western Canadian crudes are well characterized using the data available in the public realm.

PRELIM requires the characterization of the crude properties for nine crude fractions (Figure 3). The scheme of separating the whole crude into nine fractions is adopted in order to get the flexibility in modeling different refinery configurations. For example, PRELIM provides the flexibility to route each of the four crude gas oil fractions (i.e., AGO, HVGO, LVGO, and Coker GO) to hydrocracking and/or FCC process units in a different proportion (e.g., route 50% of the crude atmospheric gas oil fraction to FCC and 50% to hydrocracking). This requires that the assay data obtained be transformed prior to use in PRELIM. The assay data available to represent each crude varies among data sources. For example, CCQMP provides information for only four crude fractions and does not include hydrogen information. Major oil companies usually provide data for similar, if not different, number of crude fractions but at different cut temperatures. Confidential data may provide more detailed information, but the crude fractions are narrower than the data required by PRELIM (up to 15 crude fractions can be analyzed with standard techniques). This section details how the assays can be transformed into the PRELIM format as well as the assumptions that are required to obtain all information needed (i.e., 62 parameters associated with the five crude oil properties). The methods used for validating/verifying/evaluating the final data are also explained. Table 8 shows the property ranges (presented as minimums and maximums) for each crude oil fraction of the PRELIM crude assay inventory and illustrates the 62 parameters needed (white dotted cells). As mentioned in section 2.3.2.4 several new assays from different companies (including BP, Chevron, ExxonMobil, Statoil, and Knovel) have been added to the assay inventory of the current version of the model with the companies' permission. This section describes the transformation techniques used to characterize Western Canadian crudes using CCQMP data as they were developed on PRELIM initial version, which cover all type of transformations used so far for the assay inventory development. For other crudes and data sources all or a set of these techniques are used as required based on data availability.

Table 8: Property ranges for each crude oil fraction of the PRELIM's crude assay inventory

Description	Range	Whole Crude	LSR	Naphtha	Kerosene	Diesel	AGO	LVGO	HVGO	VR	AR
Sulphur (wt%)	Min	0.0900	0.000	0.000	0.0100	0.0500	0.0900	0.180	0.310	0.100	0.220
	Max	5.14	0.310	0.980	2.17	2.98	3.54	4.18	4.90	8.55	7.47
Nitrogen (ppm)[a]	Min	350	0.00	0.00	0.00	35.0	194	514	1002	321	872
	Max	4600	0.00	9.00	152	733	1390	2203	3116	7077	5709
API gravity	Min	7	35	35	28	22	17	12	7	-1	1

	Max	39	105	76	41	33	29	25	22	14	40
Density (kg/m3)	Min	828	598	682	819	860	882	901	921	969	824
	Max	1019	848	848	887	924	953	988	1022	1111	1111
Hydrogen (wt%)	Min	10.1	12.2	12.2	12.0	11.6	11.1	10.3	9.6	8.0	8.7
	Max	13.2	18.9	15.5	13.3	13.4	12.9	12.6	12.2	13.8	12.8
MCR (wt%)	Min	0.02								1.72	
	Max	14.7								32.0	
Approximated Kw	Min	11.0	10.7	10.9	11.1	11.1	11.0	10.9	10.9	10.6	10.6
	Max	12.2	13.9	12.4	11.8	11.8	11.9	11.0	12.0	11.8	12.0
Tb(50%) weight basis (ᵒC)	Min	296	26	111	221	302	360	404	452	534	203
	Max	467	214	214	276	326	377	431	493	687	700
Mass fraction yield(%)	Min	100	0.00	0.00	1.70	4.80	6.00	7.00	5.00	1.00	19.0
	Max	100	8.00	21.0	26.4	20.0	26.0	26.0	15.9	59.3	83.7
Volume fraction yield(%)	Min	100	0.00	0.00	2.00	5.00	6.00	6.76	4.48	0.881	17.3
	Max	100	12.2	22.0	28.8	19.5	25.6	25.0	16.4	56.7	82.0

[a] Note: Current version of PRELIM uses nitrogen only for information purposes. White cells highlight the 62 parameters needed and associated with the five crude properties. Atmospheric Residue: AR. Vacuum Residue: VR. Atmospheric Gas Oil: AGO, Light Vacuum Gas Oil: LVGO, and Heavy Vacuum Gas Oil: HVGO

5.5.1 Transformation methods

Four sets of calculations are used to estimate the crude quality parameters from publicly available assay data: 1) average crude distillation curves, 2) regression analysis between the fraction properties and a single fraction characteristic boiling point (i.e., a single value of boiling point that represents the boiling temperature range specific to each crude fraction) to determine crude fraction API and sulphur, 3) empirical correlations to determine hydrogen content of crude fractions, and 4) approximations for the characterization of the heaviest crude fractions that include determining carbon residue content. Five years of average data for each crude are used to account for seasonal variation in the quality of conventional crudes and OS products. The transformation methods have been evaluated using more than 50 confidential assays (assays include crudes which sulphur content and API of the whole crude range from 0.023 wt% to 5.4 wt% and API range from 10.3 to 44.9 respectively) and the final parameter values are evaluated in a assay co-validation exercise (section 4.1.2 provides the assay co-validation methods and section 4.3 provides their results and analysis).

5.5.2 Canadian crude quality monitoring program data

CCQMP offers two types of assay data: it provides simple (less costly/easy measurement) assay information that includes distillation curves determined by a gas chromatography method (High Temperature Simulated Distillation - HTSD) and the assessment of the whole crude API, sulphur, nitrogen, and MCR content. It also has more detailed assay information that includes crude fraction yield analysis by using real distillation methods (ASTM D2892/D5236) and subsequent analysis of sulphur content, nitrogen content, and API properties of the crude fractions. A set of cut temperatures (i.e., the boiling temperature ranges that must be specified to separate the crude into its fractions) has been standardized by CCQMP to analyze only four fractions: Naphtha at 190°C,

Distillate at 343°C, Gas Oil at 527°C, and Residue at a temperature beyond 527°C (i.e., 527+°C) (CCQMP): the data result from analyzing monthly samples for each crude. Most crudes are tested to obtain the simple assay information, but not all of them get the more detailed analysis. At the time of validation described in section 9 (2010-2012), the PRELIM assay inventory used the data for 22 crudes where both types of assay data were provided at the time of the data collection (November 2009).

5.5.3 Average crude distillation curves

PRELIM crude assay inventory uses the distillation curve information derived from the HTSD method. The information is used for determining specific crude fraction yields and the single characteristic boiling point for the range within each fraction. The data obtained by the HTSD method are selected over the real distillation information due to its level of resolution; specifically, it reports the temperature at which each incremental wt% of the crude is recovered. The data therefore allow the flexibility to determine the crude fraction yields at any set of cut temperatures. In addition, it allows for the determination of the single fraction characteristic boiling point. The latter is required in further characterization of the crude (i.e., use of empirical correlations to determine hydrogen content and regression analysis methods to derive API and sulphur content of each fraction).

5.5.3.1 Crude fraction yields

PRELIM uses information about crude fraction yields on mass and volume units at nine cut temperatures (Figure 3). The cutting scheme is not unique, and in real-world operations the boiling temperature ranges of each crude fraction can vary based on desired refinery products (Gary et al., 2007). The mass yield of each fraction is determined after average HTSD temperature data at each 1wt% incremental mass yield, and the cumulative mass yield of the low end of the fraction boiling temperature range is subtracted from the cumulative mass yield of the high end of the fraction boiling temperature range. The volume yield of each fraction is calculated as the fraction mass yield times the crude fraction density. In industry, there are several empirical correlations that convert distillation curve data to different measurement units. Ideally, the distillation curve data on a mass basis would be transformed to a volume basis using one of these correlations, because it would have dealt with the issues associated with predicting crude fraction density (section 5.5.4). However, to the knowledge of the authors, there is no empirical correlation that relates HTSD data to other methods of measurement that report the crude fraction yields and boiling points on a volume basis (empirical correlations among other distillation curves are available in Riazi [2007]). One possible reason is that though the cumulative statistical error of the HTSD method, as compared with ASTM methods (D2892/D5236), is acceptable ("the relative SDs of the total percent recoveries of material in the range <720°C ... ranged from about 1% to 5% for the different crude oils tested"), the HTSD method is still under investigation to be accepted as a standard by the industry (Villalanti et al., 2000).

5.5.3.2 Single fraction characteristic boiling point

In the construction of the PRELIM assay inventory, a single fraction characteristic boiling point is consistently used in the empirical correlations available for crude fraction hydrogen content and enthalpies as well as for calculating the Kw factor and conducting regression analysis. The use of a single value boiling point that represents the boiling temperature range of a crude fraction is a common approach in the industry. This approach can be applied in different ways that differ in how the characteristic boiling point of a crude fraction is calculated. Ideally, the characteristic boiling point should account for differences in the ratio of specific gravity to molecular weight among hydrocarbons (molar average boiling point) (Watson et al., 1933) and have additive characteristics in a mixture (i.e., account for both the weight fraction/contribution of each component in the mixture and the molar

average boiling point known as mean average boiling point) (Smith et al., 1937). In practice, several definitions for a single fraction characteristic boiling point appear based on the type of information available. For example, one fraction characteristic boiling point can be the fraction volume average boiling point. This boiling point on a volume basis can be calculated by distilling the crude fraction using a standard distillation test (ASTM D86/ASTMD1160), and averaging the temperatures at 10, 30, 50, 70, and 90% volume yields of the fraction (Riazi, 2007). In the documentation, the single fraction characteristic boiling point corresponds to the temperature that represents 50% of the mass yield of each fraction ($Tb_{wt50\%}$ on mass basis). There is a need to recognize that because the HTSD represents the whole crude distillation curve, this approach may neglect the deviations that exist between each crude fraction distillation curve and the whole crude distillation curve. However, the measurement of the effects of this approach was out of the scope of this documentation.

5.5.4   Regression analysis

Regression analysis between the fractions properties and the single fraction characteristic boiling point is recognized as a method in industry to predict properties of the crude at different cut temperatures (Riazi, 2007; Maples, 1997). Regression analysis is carried out in order to determine sulphur content and API of each fraction based on its $Tb_{wt50\%}$. A specific regression analysis is conducted for each crude and crude property. For example, for Albian Heavy Synthetic crude, the sulphur content of a fraction is calculated by the expression:

$$S\ wt\% = 5.65 \times 10^{-08}\ (Tb_{wt50\%})^3 - 5.33 \times 10^{-05}(Tb_{wt50\%})^2 + 2.10 \times 10^{-02}(Tb_{wt50\%}) - 1.72.$$

The expression results from using the property values of each fraction assessed from the real distillation analysis and the single fraction characteristic boiling point $Tb_{wt50\%}$ derived from the HSTD. The third polynomial regression form results from plotting the API and sulphur values for each crude fraction against its $Tb_{wt50\%}$, where the data exhibit a polynomial trend. The third-order polynomial regression fits most crudes (coefficient of determination 0.99 or higher), except for synthetic crude oils (section 5.5.6). The average of the properties of the whole crude from samples analyzed by HTSD is checked against the average and standard deviation of such properties from samples analyzed by the real distillation analysis to validate if the results are consistent.

5.5.5   Empirical correlations for determining hydrogen content of crude fractions

Crude fraction $Tb_{wt50\%}$ and API properties are used to predict the hydrogen content of each crude fraction. The hydrogen content of the lighter fractions of the crude (i.e., LSR, Naphtha, and Kerosene) are predicted using the Goossens correlation (Goossens et al., 1997). The correlation requires density, refractive index, oxygen content, and molecular weight data for the crude fractions; current assay inventory neglects effects of oxygen content (an alternative when using the correlation) and combined the Goossens hydrogen correlation with the Goossens molecular weight correlation (Goossens et al., 1997; Goossens et al., 1996) to determine (by trial and error calculation) the hydrogen content using only crude fraction $Tb_{wt50\%}$ and API. The hydrogen content of the remaining heavier fractions is predicted using the Choudhary correlation (Choudhary et al., 2008), which also only requires the crude fraction $Tb_{wt50\%}$ and API. There is a concern in using Goossens hydrogen correlations for the lighter fractions since most of the fractions that Goossens used to develop the correlations are heavy gas oils, extra heavy gas oils, or hydrocracked vacuum gas oils. Also, the fractions that Goossens used for correlation development are low in sulphur, relative to fractions from bitumen or bitumen-containing crudes. However, the correlations outlined in Goossens are used since other simple methods are not found to estimate hydrogen content of the lighter fractions. The Choudhary correlation is tested using 22 confidential assays that included hydrogen content of heavy fractions. It is confirmed that the Choudhary correlation works well for most of the

heavy fractions, and underestimates hydrogen content of the heaviest fractions (565°C+) by approximately 5%. The co-validation process confirmed the appropriateness of using both Goossens and Choudhary correlations (section 9.1).

5.5.6 Approximations for characterization of heaviest crude fractions

The main challenge in characterizing the heaviest crude fractions (i.e., distillation residue fractions: atmospheric and vacuum distillation residues) is to determine their API or density and carbon residue content. Characterizing crude fractions is not a straightforward procedure. Sophisticated methods such as the use of pseudocomponents and/or probability distributions can be used. For the heaviest fractions, "these methods are more accurate than the use of bulk properties for the estimation of various properties" (Riazi, 2007). For current assay inventory, the mass yield of atmospheric and vacuum distillation residues is determined from the HTSD data. The data are suitable to be used because the HTSD method can determine boiling range distribution of hydrocarbons to a final boiling point of about 750°C (Villalanti et al., 2000); PRELIM final cut temperature is below that value (i.e., 525+°C). The sulphur content of the heaviest fractions is estimated through mass balance using whole crude sulphur content and the estimates of sulphur content in the light and medium crude fractions. In turn, these latter estimates are calculated using the polynomial regression analysis between the sulphur content of the crude fractions and their single fraction characteristic boiling point (section 5.5.4). In addition, the use of Choudhary correlation based on $Tb_{wt50\%}$ and API to determine hydrogen content is found to underestimate hydrogen content of heaviest fractions by 5%. It is considered an acceptable margin of error in hydrogen content estimates.

5.5.6.1 API of heaviest fractions (atmospheric and vacuum distillation residues)

Alternative approximation methods are sought to determine the API or volume yield of the distillation residue fractions. For most crudes, the methods involve neglecting volume changes that arise from mixing and approximating the fraction volume yield to the whole crude volume minus the volume yield of other crude fractions. They also include changing or approximating PRELIM final cut temperature using the CCQMP final cut and characterizing the vacuum residue fraction with the average real distillation data without any transformation. Differences between the alternative calculations are found for the sulphur and API estimates specific to each crude. The deviation between the use of the regression coefficients and the alternative calculations in the estimates of density, mass yield, and hydrogen are not higher than 8%, 9%, and 15% respectively. These results are comparable with results from the assay co-validation method (section 9.1).

5.5.6.2 Approximation for carbon residue content of the heaviest crude fraction

McKetta (1993) states that 90% of the total MCR of the whole crude is present in non-distillable residue fractions or fractions with a characteristic boiling point over 690°C. In PRELIM assay inventory the vacuum residue is defined as the fraction of the crude that boils above 525+°C. Using the HTSD data, it is estimated that the "$Tb_{wt50\%}$" of the vacuum residue fraction is around 600°C (the final boiling point of the fraction is assumed to be the final temperature reported for each crude by the HTSD method). Therefore, for current assay inventory it is assumed that most of the MCR of the whole crude (approximately 99.9%) is present in the vacuum residue fraction. The review of the 57 additional confidential assays helps to confirm that the assumption is reasonable (i.e., the percentage of MCR of whole crude in the vacuum residue fraction is comparable to the percentage reported in the assay inventory for a crude with similar whole crude API and sulphur content that the cut fraction). The assay co-validation exercise shows that the approximation is appropriate for most crudes (section 9.1).

5.5.6.3 Bottomless SCO

Most of the light SCO produced in oil sands (OS) upgrading operations is "bottomless" (do not have any vacuum residue material in it). However, CCQMP HSTD data report that up to 6wt% of the whole crude is above the cut temperature specified in the PRELIM crude assay inventory for the vacuum residue (525+°C) (this material may be associated with the material remaining in transportation pipelines). A third data point, the detailed assay information from CCQMP real distillation, does not report properties for this fraction. Therefore, it is difficult to determine whether characterization of the light SCO crudes should include vacuum residue yields and properties. Confidential assays report a fraction of material that boils over 490°C, but they do not report how much boils over 525°C (the PRELIM cut temperature for vacuum residue). Using PRELIM cut temperatures to define the presence of vacuum residue, the industry assay database used in the assay co-validation exercise (section 7.2) reports a vacuum residue fraction for light SCO assays.

Therefore, PRELIM light SCO assays include a vacuum residue fraction. Because there are few data points available from the assays in the public realm, it was not possible to get a good fit of the data using the polynomial regression method for the purposes of predicting API and sulphur content of the fractions. Therefore, an exponential regression form is applied. The comparison of the estimates using the exponential form versus a polynomial regression derived from the SCO confidential assay (API and $Tb_{wt50\%}$ data are available for 15 narrower cut temperatures) shows that the API of the first six SCO fractions is underestimated by 2 to 9% and the API of the heavy vacuum gas oil fraction is overestimated by 16%. The assumption about MCR content of the heaviest fraction is also applied to the light SCO assays. The confidential assay shows that this approximation may provide a value for the MCR of the SCO vacuum residue fraction close to the measured value for all the fraction of material that boils over 490°C of the light SCO (underestimated by only in one percentage point). The assay co-validation shows a large deviation in the MCR value of the same fraction. Effects of these assumptions are discussed in section 0.

5.5.7 Approximated Watson characterization factor

Kw definition uses the "mean average boiling point" as a single fraction characteristic boiling point instead of the $Tb_{wt50\%}$ to represent the structural composition of a crude fraction (as discussed in sections 5.3.3 and 5.5.3). Several alternative calculation methods are used to explore the effects of this approximation which included: 1) crosschecking the estimated Kw values with values reported in confidential assay information, and 2) using confidential assay information to calculate the sensitivity of the Kw parameter to using a characteristic boiling point on mass or volume basis. The estimated Kw value may change in the second or first decimal place due to changes in the use of a mean average boiling point, a $Tb_{wt50\%}$, or a $Tb_{50\%}$ on volume basis. However, the estimated Kw value may change by one unit (e.g. 11 to 12) when accounting for the standard deviation in the $Tb_{wt50\%}$ resulting from the five-year average HTSD distillation data. This suggests that the approximation may have a negligible effect when compared to the variation that could derive from upstream blending decisions that affect the crude distillation curves. The assay co-validation exercise shows that the estimated Kw values in PRELIM crude assay inventory are consistent with the values reported from a more comprehensive crude assay database (section 9.1).

6 Process Unit Default Specifications

In PRELIM, the calculations for each process unit are based on a set of default specifications, assumptions, and a database derived from discussion with technical experts and peer-reviewed literature (as described in sections 4.1 and 5).

The data and constants used in PRELIM calculations are classified into three main areas:

- The `CokingRefineryControls` and `HydroRefineryControls` worksheets include expert inputs on swings (flow splitters that distribute flows between process units). These inputs feed `RefineryCalcs` worksheets and are used for expert modelling; data should not be modified as all the structure of the model relies on those specifications.
- The `CokingRefineryCalcs` and `HydroRefineryCalcs` worksheets that include expert inputs on intermediate process product yields (default specifications) and input data highlighted with a red background which can be overridden by expert users in the `Constants` worksheet.
- The `Constants` worksheet that organizes other data and constants information that support model calculations. Within this worksheet, only cells highlighted with a red background can be overridden by expert users.

This section provides PRELIM modelling details at the process unit level for each of the two major refinery modelling structures/calculation sets: the coking and the hydrocracking refineries. First, the default specifications and assumptions used to model each process unit based on expert input and contained within the `RefineryCalcs` worksheets are provided. Then, other assumptions and data base created based on peer-reviewed literature and contained in the `Constants` worksheet are described.

6.1 Summary of description of process units' operating characteristics in PRELIM

The following table presents a summary of the process units' purpose and specifications per type.

Table 9: Summary of description of process units' operating characteristics in PRELIM

Process	Feed	Purpose	Products	Parameters that define actual yield and products distribution	PRELIM Assumptions for yield and products distribution estimates[a]	Origin of energy requirements and particular considerations[b]
Crude distillation	Whole crude to atmospheric operations, atmospheric residuum to vacuum operations	Separate crude in fractions of different boiling range	Straight-run fractions (SRF): naphtha, kerosene, diesel, gas oils, residue.	Boiling curve of whole crude Cut temperatures	Average TBP for each crude at a specified cut temperature Sulphur distribution on SRF and estimates of SRF API unique for each crude	Heating crude until required temperature to cause vaporization of products and stripping steam to separate light ends from each distillation products. Heat is exchanged

Process	Feed	Purpose	Products	Parameters that define actual yield and products distribution	PRELIM Assumptions for yield and products distribution estimates[a]	Origin of energy requirements and particular considerations[b]
						between feed, products, and reflux increase energy efficiency and reduce energy requirements.
Reforming and isomerization	Naphtha fractions boiling above 204oC, previously hydrotreated for catalyst protection.	Modify the structure of the hydrocarbons in the lighter fractions to increase gasoline octane by isomerization and cyclization reactions: Paraffins to naphthenes, naphthenes to aromatics	Reformate: hydrocarbons components of high octane for gasoline Hydrogen Light gases from some hydrocracking reactions	Process severity: Temperature, pressure, catalyst, and feed properties Correlations based on RON number and Kw or RON number and aromatics and naphthenic content.	Feed hydrotreated to same hydrogen content and no change in boiling point; therefore, similar Kw and similar yields. Yield of light gas production (22wt%H content) 10 wt% of the hydrocarbon feed in reformer and 1%wt in Isomerization. Reformate calculated by carbon and hydrogen balance.	Endothermic dehydrogenation reactions. Negligible hydrogen to minimize carbon deposits on catalyst
Hydrotreating	Straight run fractions from crude distillation processes	Reduce content of S and N and saturate olefins or aromatic rings of distillate fuels without change their boiling range to meet specifications of feedstock for further processing, or specifications of end products (i.e. increase H/C ratio).	Saturate hydrocarbon, hydrogen sulphide, light gases	Product yield expected from 95 to 98% volume on feed.	Yield 0.2%wt liquid feed rate hydrocarbon gas with hydrogen content of 17-21%wt.	Preheating feedstock Stripping steam hydrogen rich gas
Fluid catalytic cracking	Gas oils	Increase the yield of lighter products from heavier gas oil fractions.	Light gases: C1 to C4 with high olefin content. High octane Gasoline Light	Reaction temperature, type and activity of the catalyst, ratio of catalyst mass	Correlation based on 75% conversion and 11.8 Kw factor using zeolite catalyst. Full	Heat balance is possible due to endothermic cracking reactions and exothermic

Process	Feed	Purpose	Products	Parameters that define actual yield and products distribution	PRELIM Assumptions for yield and products distribution estimates[a]	Origin of energy requirements and particular considerations[b]
		Mostly benefit gasoline yields.	and heavy cycle gas oils.	per feed mass, and contact time Hydrogen content of process feed.	hydrotreating of FCC feed[c].	catalyst regeneration Steam stripping
Hydrocracking	Kerosene, diesel, Gas oils or residuum	Increase the yield of lighter products from heavier fractions. Mostly benefit diesel yields.	Light gases: C1 to C4 Gasoline and or kerosene, and or diesel	Reactor pressure, catalyst contact time, type and activity of catalyst, and type of feed	Correlation based on feed Kw and approximated hydrogen consumption Products are routed as follow: C3 and lighters to refinery fuel gas, C4 and fractions below 204 oC (400 oF) to gasoline, and the rest of the material that boils above the gasoline cut temperature, can be used either as jet fuel or diesel	Hydrogen rich gas Excess of heat may be produced due to high exothermic hydrogenation reactions versus low endothermic cracking reactions
Delayed coking	Vacuum residuum (VR) or FCC heavy gas oils	Increase the yield of lighter products from heavier fractions. Prepare FCC and HC feedstock. FCC heavy gas oils are used to produce needle coke.	Coke Light gases: C1 to C4 Naphtha Gas oil	Heater outlet temperature, fractionators' pressure, vapours' temperature, and "free" carbon content	Correlation based on "free" carbon content (measured by micro carbon residuum) and API of the feed. Correlation was derived for feed under 18 API and straight run products (VR)	Thermal cracking process Steam stripping Decoking system

S: Sulphur content; content; H: Hydrogen content; ~Kw Watson characterization factor; wt: weight basis.[a] Products specifications assumptions in Table 10

[b] Energy requirements assumptions in Table 5 and Table 4
[c] FCC Conversion: 100 (volume of feed - volume of effluent not converted to naphtha and lighter products)/ volume of feed. The model assumes conversion of 75% suggested for high boiling feed.

Table 10: PRELIM assumptions on refinery intermediate products specifications

Intermediate Product	API / Density (kg/m³)	Sulphur (wt%)	Hydrogen (wt%)
Distillated Fractions	Crude assay inventory	Crude assay inventory	Crude assay inventory
Hydrotreated Naphtha	CAI[a] +1 API [1]	0	Linearly correlated with input H%
Hydrotreated Kerosene	41 / 820	0	Linearly correlated with input H%
Hydrotreated Diesel	40 / 825	11 ppm	Linearly correlated with input H%
Keromix Product	41 / 808	0	13.8
Coker naphtha	52 / 770	S, FCDP [b]	12.0
Coker gas oil	20 / 934	S, FCDP [b]	11.0
Coke	n.a.[c]	n.a.[c]	5.9
Hydrotreated Coker Naphtha	60 / 740	0	Linearly correlated with input H%
Hydrotreated Hydrocracking Naphtha	65 / 720	0	Linearly correlated with input H%
Hydrotreated FCC Feed	24 /910	0	Linearly correlated with input H%
FCC LPG	FC [d]	S, FCDP [b]	16.1
FCC Gasoline	FC [d]	S, FCDP [b]	Linearly correlated with input H%
FCC LGO	FC [d]	S, FCDP [b]	9.8
FCC HGO	FC [d]	S, FCDP [b]	8.0
FCC Coke	n.a [c]	S, FCDP [b]	5.9
Reformate	52 / 770	n.a [c]	12.3
Hydrogen from Naphtha Catalytic Reformer	n.a [c]	n.a [c]	100
Alkylate	73 / 693	n.a [c]	n.a [c]
HC Products	FWF [e]	Feed's S 100% to HC Fuel oil	FWF[e] and 17.2 for iC4&nC4

[1] Maples, R., *Petroleum Refinery Process Economics.* Second ed.; PennWell Corp: 2000.

[a] CADI: Crude Assay Inventory

[b] FCDP: Process Feed Content of sulphur (S) Distributed in process's Products. Gary et al. (2007) give figures that show S distribution in process's products as function of the S present in the process' feed.

n.a [c] No applicable to PRELIM model calculations.

[d] FC: Function of Conversion. Gary et al. (2007) give figures that show FCC product's density as function of conversion: 100 (volume of feed - volume of effluent not converted to naphtha and lighter products)/ volume of feed. This study, assumed conversion of 75% suggested for high boiling feed (see Sensitivity FCC Performance Assumptions section for further details).

[e] FWF: Function of Watson characterization Factor. Gary et al. (2007) give figures that show characterization factor and hydrogen content of hydrocracking products as function of average mid boiling points. The density was calculated (see section Approximated Watson characterization factor). and hydrogen specified from these factors and assumptions on average mid boiling points This study, assumed Gary et al. suggested average mid boiling points of 55, 138, and 238 °C for the hydrocracking products and uses figures for zeolite catalyst. Gary et al. (2007) give figures that show yields as function of API and hydrocracking severity. This study uses yields derived from assuming a hydrocracking severity of 1500 scf H/bbl.

6.2 Configurations common to the coking and the hydrocracking refinery

This subsection provides the user with an overview of the configurations and each process unit common to the two main refinery modelling structures/calculations sets, including:

- Process flow diagrams;
- A general description of the process unit purpose and function;
- The list of all (active and potential) input and output streams – this includes the swings that can be modified to change the destination of streams (note: power is necessary for operation of all process units, and is not specifically mentioned as an input); and
- Calculations in PRELIM specific to each process unit, including the assumptions tied to the calculations and the equations used. These processes are detailed in the order they are presented in `CokingRefineryCalcs` and `HydroRefineryCalcs` worksheets.

6.2.1 Process flow diagrams

The following figures provide a process flow diagram and a short description for each of the four refinery configurations common to the two major refinery modelling structures modelled in PRELIM.
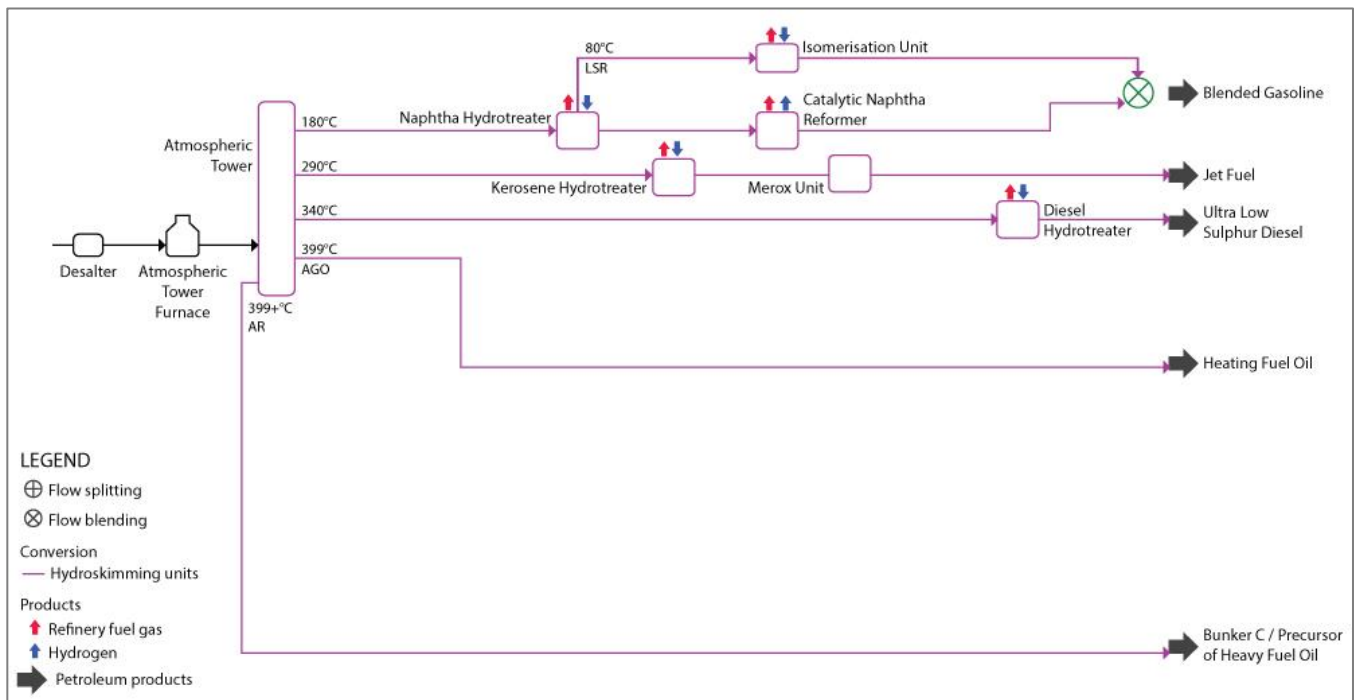
Figure 14: Configuration 0

Only the hydroskimming process units are enabled in configuration 0.
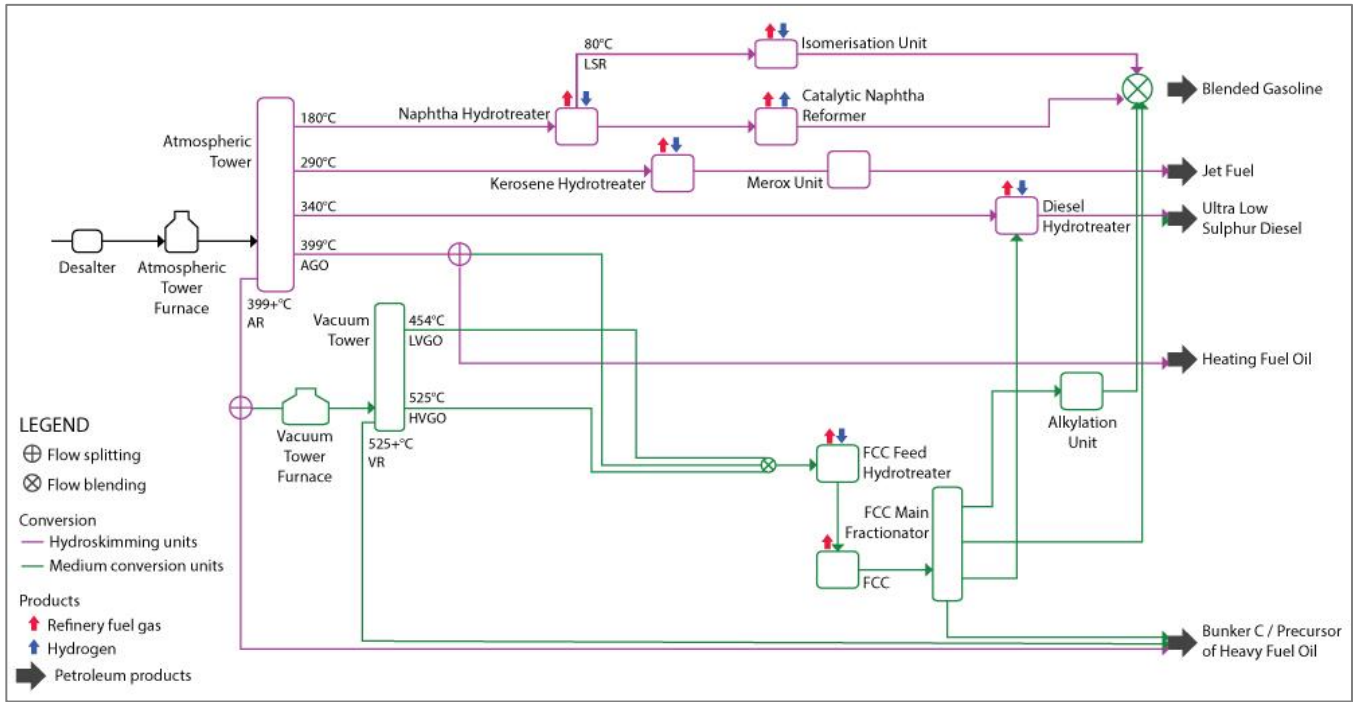
Figure 15: Configuration 1

In configuration 1, the hydroskimming process units as well as the process units associated with the fluid catalytic cracker (FCC) are enabled to provide a medium conversion.
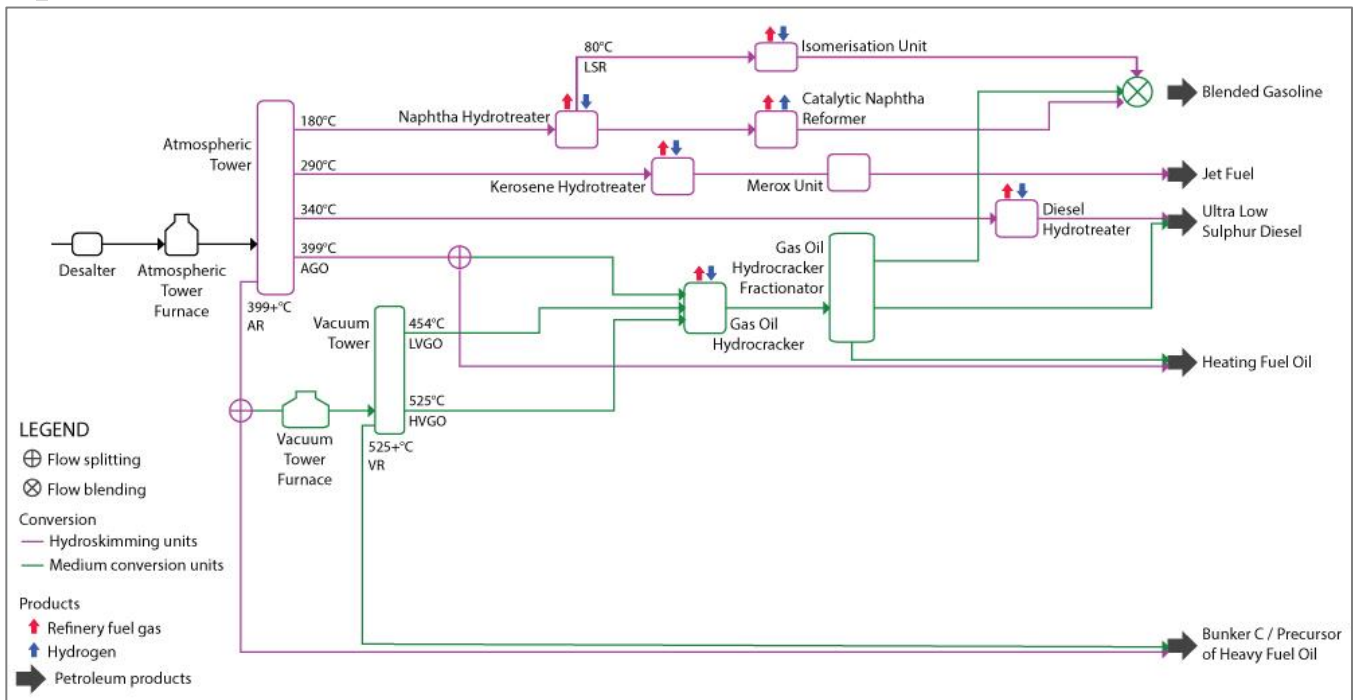
Figure 16: Configuration 2

In configuration 2, the hydroskimming process units as well as the process units associated with the gas oil hydrocracker are enabled to provide a medium conversion.
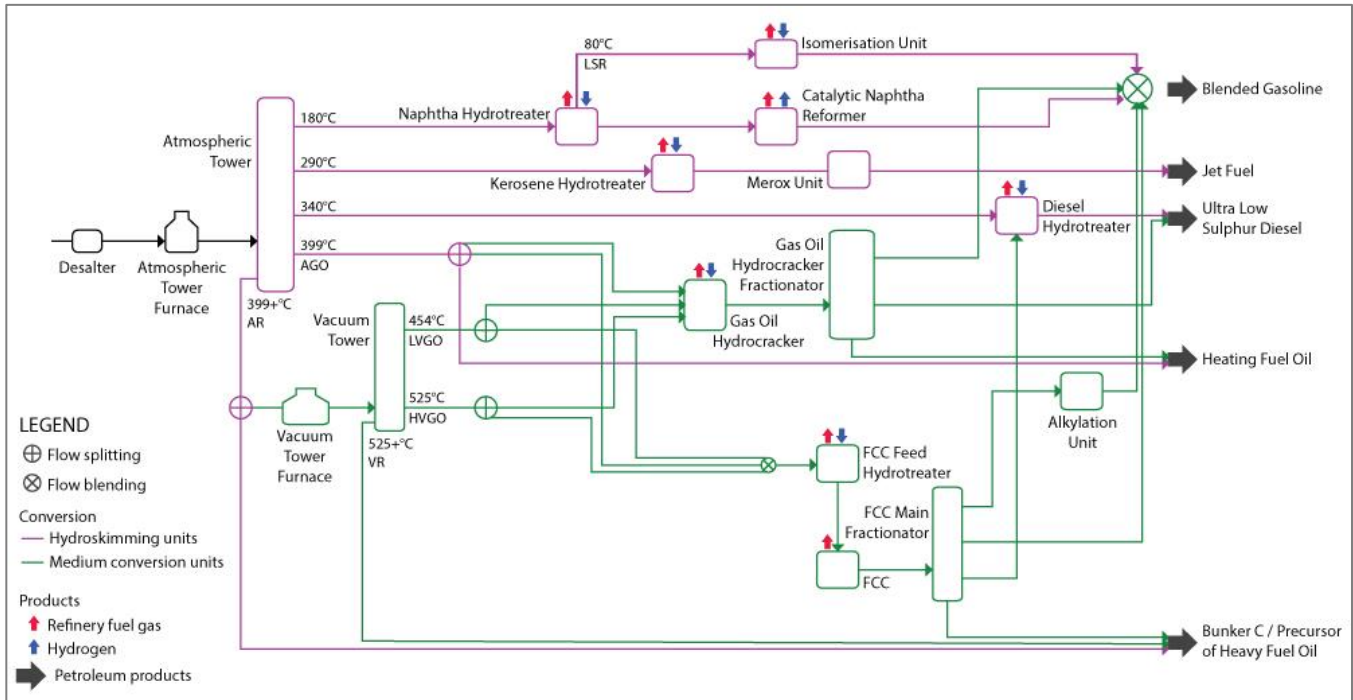
Figure 17: Configuration 3

> In configuration 3, the hydroskimming process units, the process units associated with the gas oil hydrocracker, and the process units associated with the fluid catalytic cracker (FCC) are enabled to provide a medium conversion.

6.2.2 Process units in the hydroskimming configuration

6.2.2.1 Desalter

6.2.2.1.1 Process unit description

This unit is the first unit that crude oil passes through in a refinery. Its purpose is to remove the salt present in crude oil.

6.2.2.1.2 Output

The desalted crude oil is sent to Atmospheric Tower Furnace.

6.2.2.1.3 Calculations

6.2.2.1.3.1 Stream processing

PRELIM does not consider the mass of the salt that is removed, as the value and effect on the calculations are negligible. This explains the fact that the output stream has the same properties as the input stream that are considered in the model. However, the energy used for desalting the crude is considered.

6.2.2.2 Atmospheric Tower Furnace

6.2.2.2.1 Process unit description

This unit preheats the crude stream before it enters atmospheric tower.

6.2.2.2.2 Input

The input stream comes directly from the desalter unit.

6.2.2.2.3 Output

Once preheated, the output stream is sent to atmospheric tower.

6.2.2.2.4 Calculations

The energy consumption of the unit is calculated based on the volume of gas required to heat the volume of crude oil passing through the unit.

6.2.2.2.4.1 Equation

The calculation is performed based on the enthalpy of the input and output streams, using the following equation (Moharam et al., 1998):

$$H_L = [0.03181T + 0.00001791Kw^{4.693}]^{2.2916}$$

Where:

H_L is the enthalpy of the stream (kJ/kg)

T is the temperature in Kelvins

Kw is the characterization factor

6.2.2.3 Atmospheric Tower

6.2.2.3.1 Process unit description

Atmospheric tower is the first major unit met by crude oil and the most important one in a refinery. In this unit, crude oil molecules entering the tower are separated based on their boiling points. Lighter molecules evaporate and travel to the top portion of the tower where they are collected, while heavier ones are collected at the bottom of the tower.

6.2.2.3.2 Input

The input stream comes from atmospheric tower furnace.

6.2.2.3.3 Output

There are five straight-run fractions (SRF) coming out of atmospheric tower. Each fraction is sent to a different process unit for further processing, based on the new properties of the fraction that are different from the original whole crude oil.

The light straight-run fractions are sent to different sections of the refinery for further processing based on their distillation cut temperature:

- Naphtha (distillation cut temperature of initial boiling point (IBP) to 180°C) is sent to naphtha hydrotreater;
- Kerosene (distillation cut temperature of 180 to 290°C) is sent to kerosene hydrotreater; and
- Diesel (distillation cut temperature of 290 to 340°C) is sent to diesel hydrotreater.

Atmospheric tower also produces two heavy fractions:

- Atmospheric gas oil (AGO, distillation cut temperature of 340 to 399°C); and
- Atmospheric residue (AR, distillation cut temperature of 399+°C).

In the hydroskimming-only configuration, AGO and AR are directly considered final products (heating fuel oil and heavy fuel oil, respectively). If the medium or the deep conversion configuration is selected, two swings are activated to process these streams further to produce higher quality products.

6.2.2.3.4 Calculations

The whole crude assay's properties are used to calculate the flow rates of outputs to each subsequent process unit for each fraction. The following assumptions are used by PRELIM to estimate yield and product distribution:

- Average temperature boiling point (TBP) at a specified cut temperature;
- Sulphur distribution of the SRF and estimates of SRF API are unique for each crude.

6.2.2.4 Naphtha hydrotreater

6.2.2.4.1 Process unit description

This hydrotreater unit uses gas, electricity and hydrogen to reduce sulphur and nitrogen content, as well as to saturate olefins or aromatic rings of distillate fuels without changing the boiling range of the fraction to meet specifications of feedstock for further processing, or specifications of end products (i.e., increase H/C ratio).

6.2.2.4.2 Input

The input stream contains light straight run naphtha (SRN) from atmospheric tower.

6.2.2.4.3 Output

This process unit produces desulphurized light gases of three types:

- Light straight run (LSR, distillation cut temperature of 80°C) is sent to the isomerization unit;
- The rest of the naphtha stream is sent to catalytic naphtha reformer or directly separated as a final product – Naphtha;
- Refinery fuel gas that can be reused within the refinery or sold as a product since it has properties close to natural gas.

6.2.2.4.4 Calculations

PRELIM assumes a product yield of 0.2%wt for liquid feed rate and refinery fuel gas hydrogen content of 18.36%wt.

6.2.2.5 The isomerization unit

6.2.2.5.1 Process unit description

The isomerization unit modifies the structure of the hydrocarbons in lighter fractions to increase gasoline octane by isomerization and cyclization reactions (i.e., paraffins to naphthenes, naphthenes to aromatics).

6.2.2.5.2 Input

Input to this process unit is the desulphurized stream coming from naphtha hydrotreater.

6.2.2.5.3 Output

This process unit produces two streams:

- Reformates, hydrocarbon components with high octane content for gasoline processed stream;
- Hydrogen light gas that can be reused as RFG within the refinery.

6.2.2.5.4 Calculations

PRELIM uses the following assumptions to process the stream:

- There is no change in boiling point; therefore, the input and output streams from this unit have similar Kw and yields.
- Yield of light gas production is 1%wt of the hydrocarbon (Gary et al. (2007)). The output stream is calculated using carbon and hydrogen balance.

6.2.2.6 Catalytic naphtha reformer

6.2.2.6.1 Process unit description

Catalytic naphtha reformer processes the input stream from naphtha hydrotreater and breaks it into lighter fractions that can be added to the gasoline pool. One of the byproducts of this unit is the associated hydrogen production.

6.2.2.6.2 Input

The desulphurized stream comes from the naphtha hydrotreater in the hydroskimming-only configuration and may be associated with a stream coming from the heavy naphtha hydrotreating unit if the deep conversion applies and heavy naphtha is selected to be treated here.

6.2.2.6.3 Output

This process unit produces three streams:

- The processed stream is sent to the gasoline pool;
- Hydrogen; and
- Refinery fuel gas that can be reused within the refinery or sold as a product since it has properties close to natural gas.

6.2.2.6.4 Calculations

PRELIM uses the following assumptions to process the stream:

- The feed is hydrotreated to the same hydrogen content as the input stream and there is no change in boiling point; therefore, the streams have similar Kw and yields.
- Yield of light gas production (22wt%H content) is 10 wt% of the hydrocarbon feed (Gary et al. (2007) and input from industry experts). Reformate stream is calculated using a carbon and hydrogen balance.

The octane number is calculated for the hydrotreated straight run naphtha as the average of research octane number (RON) and motor octane number (MON). The following calculations are currently used in PRELIM to connect assay parameters (i.e. T_{b50} and specific gravity), process unit operating severities and octane number:

Motor octane number from catalytic naphtha reformer (Baird, 1987):

$$MON = 11.38 + 0.7742 * RON$$

Note: octane number input in PRELIM is the average of RON and MON (this average is referred to as (R+M)/2)

PNA composition, Riazi-Daubert methods (Riazi, 2007):

$$x_P + x_N + x_A = 1$$

$$x_P = 3.7387 - 4.0829SG + 0.014772m$$

$$x_N = -1.5027 + 2.10152SG - 0.02388m$$

$$m = M(n - 1.475)$$

$$n = (\frac{1 + 2I}{1 - I})^{1/2}$$

$$I = 0.3773T_b^{-0.02269}SG^{0.9182}$$

Where:

$x_{P,N,A}$ is fractions of paraffin, naphthene and aromatics, respectively

M is molecular weight of hydrocarbon mixture

N is refractive index at 20°C

I is refractivity intercept

T_b is normal boiling point in Kelvin

SG is specific gravity at 60°F/15.5°C

Note: $x_A = 1 - (x_P + x_N)$. If $x_A < 0$ by this method, then $x_A = 0$, and x_P and x_N must be normalized

Reformer yields (Fahim, 2010):

$$H_2 \, wt\% = -12.1641 + 0.06134 * R \, vol\% + 0.099482 * RON_R$$

$$R \, vol\% = 142.7914 - 0.77033 * RON_R + 0.219122 * (N + 2A)_F$$

Where:

H_2wt% is weight percent H_2 of total final products

R is volume percent reformate yield

RON_R is research octane number of reformate

$(N + 2A)_F$ is sum of volume percents of naphthene content and two times aromatic content in feed

Gas requirement assumption:

The gas requirement of catalytic naphtha reformer (scf/bbl reformer input) is scaled up linearly from the constant that is assumed when H content in the reformer output is 12.3 wt%. This is based on the following assumptions: 1) the dehydrogenation reaction of the reformer is the main reaction, and is highly endothermic, and 2) this reaction accounts for almost all the net energy demand of the reformer, which is provided by gas.

6.2.2.7 Kerosene hydrotreater

6.2.2.7.1 Process unit description

Kerosene hydrotreater uses gas, electricity and hydrogen to reduce sulphur and nitrogen content, as well as to saturate olefins or aromatic rings of distillate fuels without changing their boiling range to meet specifications of fraction for further processing, or specifications of end products (i.e., increase H/C ratio).

6.2.2.7.2 Input

The input stream consists of kerosene straight run fraction coming from atmospheric tower (distillation cut temperature of 290°C).

6.2.2.7.3 Output

This process unit produces two streams:

- A desulphurized stream of the kerosene fraction that can go to jet fuel, diesel, fuel oil, and LHE; and
- Refinery fuel gas that can be reused within the refinery or sold as a product since it has properties close to natural gas.

6.2.2.7.4 Calculations

PRELIM assumes a product yield of 0.2%wt for liquid feed rate and refinery fuel gas hydrogen content of 18.21%wt (Gary et al. (2007) and input from industry experts).

6.2.2.8 Kerosene Merox unit

6.2.2.8.1 Process unit description

The Merox unit allows additional treatment to transform the hydrotreated kerosene stream into jet fuel. Merox is an acronym for mercaptan oxidation. It is a catalytic chemical process used to remove mercaptans from the kerosene stream.

6.2.2.8.2   Input

The desulphurized stream comes from kerosene hydrotreater.

6.2.2.8.3   Output

The processed stream is sent to the jet fuel pool. Mercaptans are not included in the characteristics of the crude but the energy required to remove them is estimated in the model.

6.2.2.9   Diesel hydrotreater

6.2.2.9.1   Process unit description

The diesel hydrotreater unit uses gas, electricity and hydrogen to reduce to reduce sulphur and nitrogen content, as well as to saturate olefins or aromatic rings of distillate fuels without changing their boiling range to meet specifications of feedstock for further processing, or specifications of end products (i.e. increase H/C ratio).

6.2.2.9.2   Input

The input stream consists of diesel (and sometimes straight run kerosene as well) straight run fraction coming from atmospheric tower (distillation cut temperature of 340°C). Another possible stream comes from the fluid catalytic cracking (FCC) unit if the medium or the deep conversion and FCC are both active. One other possible input stream comes from the coking or the hydrocracking unit feeds if the deep conversion configuration is active.

6.2.2.9.3   Output

This process unit produces two streams:

- The desulphurized stream is sent to the ULSD and sometimes jet fuel.
- Refinery fuel gas that can be reused within the refinery or sold as a product since it has properties closed to natural gas.

6.2.2.9.4   Calculations

PRELIM assumes a product yield of 0.2%wt for liquid feed rate and refinery fuel gas hydrogen content of 18.21%wt.

The calculated cetane index (CCI) is calculated for the HT Diesel stream as an estimate for cetane number. The following calculations are currently used in PRELIM to connect assay parameters (i.e. T_{b50} and specific gravity), process unit operating severities and cetane number:

Calculated cetane index (CCI) as substitute for cetane number (multiple sources):

$$CI = 454.74 - 1641.416D + 774.74D^2 - 0.554B + 97.803(\log B)^2$$

Where:

D is specific gravity at 15°C

B is mid-boiling point temperature (°C)

Diesel specific gravity (Baird, 1987):

$$SG_d = SG_f - 0.026H$$

Where:

SG$_d$ is specific gravity of diesel

SG$_f$ is specific gravity of diesel hydrotreater feed

H is weight percent of hydrogen consumption

6.2.3 Process units added in the medium conversion configuration

The following process units are used in addition to the preceding ones when the medium conversion or the deep conversion configuration is enabled.

> Note: PRELIM automatically chooses the "most suitable" configuration to process crude oil as a default. However, the user can override the refinery configuration on the 'Main Inputs and Outputs' worksheet.

6.2.3.1 Gas oil hydrocracker

6.2.3.1.1 Process unit description

Gas oil hydrocracker further cracks the heaviest fractions from atmospheric tower into components that can be made into higher quality products. That is, the process increases the yield of lighter products from heavier fractions. In general, it increases diesel yields.

6.2.3.1.2 Input

The input stream can have up to four origins depending on the selected configuration:

- Atmospheric gas oil (AGO, distillation cut temperature of 399°C) coming from the atmospheric tower (all configurations);
- Light vacuum gas oil (LVGO, distillation cut temperature of 454°C) coming from the vacuum tower (medium and deep conversion);
- Heavy vacuum gas oil (HVGO, distillation cut temperature of 525°C) coming from the vacuum tower (medium and deep conversion); and
- Coker or residue hydrocracker gas oil coming from the coking or residue hydrocracking unit (deep conversion).

6.2.3.1.3 Output

This process unit produces two streams:

- The processed stream is sent to the gas oil hydrocracker fractionator; and
- C3 and lighter components are routed to refinery fuel gas, to be reused within the refinery or sold as a product since it has properties close to natural gas.

6.2.3.1.4 Calculations

The required assumptions for hydrogen consumption and yield and product distribution calculations are taken from Jones (2008) and Gary et al. (2007) respectively and are shown in the `Process Correlations` worksheet.

6.2.3.2 Gas oil hydrocracker fractionator

6.2.3.2.1 Process unit description

Gas oil hydrocracker fractionator has similar functionality as atmospheric tower in that it separates the input stream into three new streams based on their quality parameters.

6.2.3.2.2 Input

The input stream comes from the gas oil hydrocracker.

6.2.3.2.3 Output

This process unit produces three streams:

- The light stream consists of C4 and fractions with boiling points below 204 °C. This stream goes to the gasoline and sometimes jet fuel;
- The medium stream boils above the gasoline cut temperature and goes to the ULSD pool;
- The heavy stream goes to the heating fuel oil pool.

The calculations of the gas oil hydrocracker fractionator yields are based on the method proposed by Gary et al. (2007).

6.2.3.3 Vacuum tower furnace

6.2.3.3.1 Process unit description

Vacuum tower furnace has similar functionality as atmospheric tower furnace in that it preheats the fuel that goes to vacuum tower.

6.2.3.3.2 Input

The input stream is the atmospheric residue coming from atmospheric tower.

6.2.3.3.3 Output

The processed stream is sent to vacuum tower.

6.2.3.3.4 Calculations

6.2.3.3.4.1 Equation

The calculation is performed based on the enthalpy of the input and output streams, using the following equation (Moharam et al., 1998):

$$H_L = [0.03181T + 0.00001791Kw^{4.693}]^{2.2916}$$

Where:

H_L is the enthalpy of the stream (kJ/kg)

T is the temperature in Kelvins

Kw is the characterization factor

This equation uses the difference between the inlet and outlet temperatures to calculate the difference in enthalpy for all fractions of the crude oil.

6.2.3.4   Vacuum tower

6.2.3.4.1   Process unit description

Vacuum tower has similar functionality as atmospheric tower but operates at lower pressure and higher temperature to further crack molecules present in the input stream.

6.2.3.4.2   Input

The atmospheric residue stream comes from vacuum tower furnace, where it is preheated.

6.2.3.4.3   Output

This process unit produces three streams:

- Light vacuum gas oil (LVGO, distillation cut temperature of 454°C) is sent to a swing that distributes it to the gas oil hydrocracker and/or to the fluid catalytic cracker;
- Heavy vacuum gas oil (HVCO, distillation cut temperature of 525°C) is sent to a swing that distributes it to the gas oil hydrocracker and/or to the fluid catalytic cracker;
- Vacuum residue (VR, distillation cut temperature of 525+°C) is sent to the heavy fuel oil pool. If the deep conversion is selected, a swing allows for the rerouting of a share of the VR to the coking furnace or the residue hydrocracker furnace, depending on the configuration.
- Note LVGO and HVGO can be directly separated as a final product. See cells K549-L549 on the calculation tab and cells K40-L41 on the results single assay tab.

6.2.3.5   Fluid catalytic cracking hydrotreater

6.2.3.5.1   Process unit description

This hydrotreater unit uses gas, electricity and hydrogen to reduce sulphur and nitrogen content, as well as to saturate olefins or aromatic rings of distillate fuels without changing the boiling range to meet specifications of the stream for further processing, or specifications of end products (i.e., increase H/C ratio).

6.2.3.5.2   Input

A swing allows mixing streams from up to four sources, depending on the selected configuration:

- LVGO from vacuum tower (medium and deep conversion);
- AGO from atmospheric tower (medium and deep conversion);
- HVGO from vacuum tower (medium and deep conversion);
- Coker or residue hydrocracker gas oil coming from the coking or residue hydrocracking unit (deep conversion).

6.2.3.5.3 Output

This process unit produces two streams:

- The desulphurized stream passes through to the fluid catalytic cracker;
- Refinery fuel gas that can be reused within the refinery or sold as a product since it has similar properties to natural gas.

6.2.3.5.4 Calculations

PRELIM assumes a product yield of 0.2%wt for liquid feed rate and refinery fuel gas hydrogen content of 18.31%wt.

6.2.3.6 Fluid catalytic cracker

6.2.3.6.1 Process unit description

The fluid catalytic cracker (FCC) unit cracks large molecules from heavy streams into smaller molecules. It therefore increases the yield of lighter products from heavier gas oil fractions and mostly produces a stream that can be used to increase gasoline yields.

6.2.3.6.2 Input

FCC is fed by the gas oils coming from the fluid catalytic cracker feed hydrotreater unit (if the FCC post-hydrotreater option is active, flow still passes through the feed hydrotreater but with no treatment at all).

6.2.3.6.3 Output

This process unit produces two streams:

- Light gases and light and heavy cycle gas oils are directed to the FCC main fractionator;
- Refinery fuel gas that can be reused within the refinery or sold as a product since it has properties close to natural gas.

6.2.3.6.4 Calculations

Yields and products distribution estimates are calculated based on the method proposed by Gary et al. (2007) with input of industry experts. Full hydrotreating of FCC feed based on linear correlation with input H% is also assumed.

6.2.3.7 Fluid catalytic cracking main fractionator

6.2.3.7.1 Process unit description

The FCC main fractionator is similar to the atmospheric tower as it separates the incoming stream into three streams based on the properties of the fractions.

6.2.3.7.2 Input

The stream of light gases and light and heavy cycle gas oils comes from the FCC unit.

6.2.3.7.3 Output

This process unit separates the stream into four streams:

- Light gases (C1 to C4 with high olefin content) are sent to the alkylation unit;
- High octane gasoline (medium stream) is sent to the gasoline pool where it is mixed with lighter streams;
- Light and heavy cycle gas oils (heavy stream) is sent to the diesel hydrotreater where the sulphur is removed, and the stream is then added to the ULSD pool;
- The heaviest stream is sent to the heavy fuel oil pool.

6.2.3.8 Alkylation unit

6.2.3.8.1 Process unit description

This unit converts isobutene and low-molecular-weight alkenes coming from the fluid catalytic cracking main fractionator into alkylate, a high-quality gasoline component.

6.2.3.8.2 Input

The stream of light gases (C1 to C4 with high olefin content) comes from the fluid catalytic cracker main fractionator.

6.2.3.8.3 Output

The processed stream is sent to the gasoline pool where it is mixed with lighter streams and process unit calculations are based on energy consumption assumptions from the literature (Gary et al., 2007; Maples, 2000; Parkash, 2003).

6.2.3.9 Gasoline blending

Although this process unit is not explicitly displayed on the `PFDs` worksheets, it is modelled and detailed in the `calculation` worksheets.

6.2.3.9.1 Process unit description

The gasoline pool gathers and mixes gasoline streams coming from various process units.

6.2.3.9.2 Input

Gasoline streams may come from up to five process units, depending on the selected configuration:

- The isomerization unit (all configurations);
- The gas oil hydrocracker fractionator (medium and deep conversion);
- The catalytic naphtha reformer (all configurations);
- The alkylation unit (medium and deep conversion); and
- The fluid catalytic cracking main fractionator (medium and deep conversion).

6.2.3.9.3 Output

The output is blended gasoline.

6.2.3.9.4 Calculations

6.2.3.9.4.1 Stream processing

Incoming streams (iC5, reformate, HT naphtha product, FCC gasoline, HC gasoline, and alkylate) are blended. Blend properties are calculated based on mass balance.

6.2.3.10 Fuel gas treatment, sulphur recovery and pollution control

Although these process units are not displayed on the `PFD` worksheets, they are modelled and detailed in the `calculation` worksheets.

6.2.3.10.1 Process unit description

These units are responsible for treating the fuel gas to remove acid gas and sulphur.

6.2.3.10.2 Input

Streams are coming from all process units generating fuel gas.

6.2.3.10.3 Output

The output is a fuel gas that is compliant with environmental regulations associated with emissions of sulphur.

6.2.3.10.4 Calculations

6.2.3.10.4.1 Amine treatment

Acid gas is removed using amine treatment. Calculations are based on Gary et al. (2007) and Jones (2008).

6.2.3.10.4.2 Sulphur removal

Sulphur is removed using the Claus tail gas treatment.

> Source used for the sulphur recovery data: *Refining Processes Handbook*, Chapter 8 p.221 to 241

6.2.3.11 Steam generation

Although this process unit is not displayed on the `PFD` worksheets, it is modeled and detailed in the `calculation` worksheets.

6.2.3.11.1 Process unit description

This unit generates steam for the refinery, using natural gas as the source of primary energy.

6.2.3.11.2 Input

Natural gas is the only input to this process unit.

6.2.3.11.3 Output

This process unit produces steam that is circulated throughout the refinery.

6.2.3.11.4 Calculations

Sources used to calculate the steam generation energy requirements are:

- Wang 2008, Spreadsheet (File Refinery Efficiency Calculations-Wang-10-07-v4-1)
- Petroleum Refining Technology and Economics p.356
- Refining Processes Handbook, p. 302

6.2.3.12 Steam methane reformer

Although this process unit is not displayed on the `PFD` worksheets, it is modelled and detailed in the `calculation` worksheets.

6.2.3.12.1 Process unit description

The steam methane reformer produces hydrogen for the refinery.

6.2.3.12.2 Input

The steam methane reformer requires two inputs: steam, and natural gas.

6.2.3.12.3 Output

This process unit produces hydrogen for seven process units, depending on the active configuration:

- Naphtha hydrotreater (all configurations);
- Kerosene hydrotreater (all configurations);
- Diesel hydrotreater (all configurations);
- Gas oil hydrocracker (medium and deep conversion);
- Coking naphtha hydrotreater (deep conversion);
- Fluid catalytic cracking feed hydrotreater (medium and deep conversion); and
- Isomerization unit (all configurations).

6.2.3.12.4 Calculations

PRELIM first calculates the hydrogen balance for all process units. It then subtracts the hydrogen supplied by the naphtha catalytic reformer. Lastly, the energy required to produce the supplemental hydrogen via the SMR unit is calculated based on the estimated natural gas, steam, and power consumption (Gary et al., 2007; Maples, 2000; Parkash, 2003; Skone et al., 2008; Spath et al., 2001).

In PRELIM, a Steam Methane Reformer (SMR) unit has been considered to produce the hydrogen that might be needed in addition to the hydrogen that is produced as a by-product in the naphtha catalytic reformer. Hydrogen has to be separated from other products of steam methane reforming. Different technologies can be employed for this purpose. In PRELIM the option to use amine CO_2 removal or Pressure Swing Adsorption (PSA) for hydrogen purification have been included.

Amine CO_2 removal for SMR relies on aqueous solutions of various alkylamines to remove carbon dioxide (CO_2) from the hydrogen and CO_2 stream produced in the SMR. The treating solution comes into contact with the hydrogen and carbon dioxide gas in an absorber containing trays or packing. Carbon dioxide is absorbed in the solution, which is then regenerated by striping. The first version of PRELIM included only the SMR with amine CO_2 removal option, and PSA was added to PRELIM v.1.2. as it is currently the most commonly used technology for hydrogen purification in SMR units. Pressure swing adsorption (PSA) is a gas separation process in which an adsorbent is used to remove impurities from the SMR reaction products and produce a hydrogen stream. Regeneration is then carried out by reducing the partial pressure of the adsorbed component. Partial pressure reduction can be accomplished rapidly by lowering the total pressure or by using a purge gas.

In a typical SMR unit that employs PSA for hydrogen purification, the reformer is fueled primarily by the PSA off-gas, thereby only a small amount of natural gas is used to supply the balance of the reformer duty. Although the plant requires some steam for the reforming and shift reactions, the highly exothermic reactions result in an excess amount of steam produced by the plant that can be used in the refinery. The steam produced can be used by other processes or exported to other facilities. The data required for the inclusion of PSA for hydrogen purification in PRELIM were taken from a hydrogen life cycle assessment study conducted by the National Renewable Energy Laboratory (2000).

6.3 Configurations and process units specific to the coking refinery

6.3.1 Process flow diagrams

The following figures provide a process flow diagram and a short description for each of the three refinery configurations specific to the coking refinery configuration when the deep conversion is selected.

Figure 18: Configuration 4

In configuration 4, the hydroskimming process units, the process units associated with the fluid catalytic cracker (FCC), and the process units associated with the coking are enabled to provide a deep conversion.

Figure 19: Configuration 5

In configuration 5, the hydroskimming process units, the process units associated with the gas oil hydrocracker, and the process units associated with the coking are enabled to provide a deep conversion.

Figure 20: Configuration 6

> In configuration 6, the hydroskimming process units, the process units associated with the fluid catalytic cracker (FCC), the process units associated with the gas oil hydrocracker, and the process units associated with the coking are enabled to provide a deep conversion.

6.3.2   Process unit descriptions

The following process units are used in addition to the preceding ones when the coking deep conversion configuration is enabled.

> Note: PRELIM automatically chooses the "most suitable" configuration to process crude oil as a default. However, the user can override the refinery configuration on the 'Main Inputs and Outputs' worksheet.

6.3.2.1   Coking furnace

6.3.2.1.1   Process unit description

The coking furnace preheats the stream before it is processed in the coking unit.

6.3.2.1.2   Input

Coking furnace is fed by vacuum residue (VR) originating from vacuum tower.

6.3.2.1.3   Output

The heated VR is sent to the coking unit.

6.3.2.2 Coking (or delayed coking unit)

> Note: calculations for the `Coking` and the `Coking Fractionator` are gathered in the same section of the `CokingRefineryCalcs` worksheet. However, they are presented separately in this documentation.

6.3.2.2.1 Process unit description

The coking unit brings the input stream to a higher temperature to crack the molecules of VR. It therefore increases the yield of lighter products from heavier fractions and prepares the coker naphtha hydrotreater, the FCC hydrotreater, and gas oil hydrocracker feedstock.

6.3.2.2.2 Input

The VR comes from vacuum tower furnace where it is preheated.

6.3.2.2.3 Output

This process unit produces three streams:

- Light gases such as C1 to C4 and naphtha gas oil are sent to the coking fractionator;
- Coke is sent to the coke pool;
- Refinery fuel gas that can be reused within the refinery or sold as a product since it has properties close to natural gas.

6.3.2.2.4 Calculations

The correlation is based on "free" carbon content (measured by micro carbon residuum, MCR) and API of the feed. The correlation was derived for feed under 18 API and straight run products (VR) and uses the following equation (Gary et al., 2007):

Coker yield = 11.29 + 0.343 x MCR

6.3.2.3 Coking fractionator

6.3.2.3.1 Process unit description

The coking fractionator separates the light gases coming from the coking unit into two streams based on the fraction properties.

6.3.2.3.2 Input

Light gases such as C1 to C4 and naphtha gas oil come from the coking unit.

6.3.2.3.3 Output

The coking fractionator produces two streams:

- Coker naphtha (light fraction) is sent to the gas oil hydrocracker for further processing; and
- Coker gas oil (heavy fraction) is sent to a swing that distributes the stream to the FCC feed hydrotreater and/or the gas oil hydrocracker for further processing.

6.3.2.4 Coking naphtha hydrotreater

6.3.2.4.1 Process unit description

Coking naphtha hydrotreater uses gas, electricity and hydrogen to reduce sulphur and nitrogen content, as well as to saturate olefins or aromatic rings of distillate fuels without changing the boiling range to meet specifications of the stream for further processing, or specifications of end products (i.e., increase H/C ratio).

6.3.2.4.2 Input

The input stream consists of the light fraction coming from the coking fractionator.

6.3.2.4.3 Output

This process unit produces two streams:

- The desulphurized stream is sent to a swing that delivers the stream to the naphtha catalytic reformer or directly to the gasoline pool depending on the selected `Naphtha catalytic reformer options` on the `Main Input & Output` worksheet. If `SR Naphtha` is selected, the output of the coker naphtha hydrotreater goes straight to the gasoline pool, and if `SR Naphtha + Heavy Naphtha` is selected, it is sent to the naphtha catalytic reformer;
- Refinery fuel gas that can be reused within the refinery or sold as a product since it has properties close to natural gas.

6.4 Configurations and process units specific to the hydrocracking refinery

6.4.1 Process flow diagrams

The following figures provide a process flow diagram and a short description for each of the three refinery configurations specific to the hydrocracking refinery when deep conversion is selected.
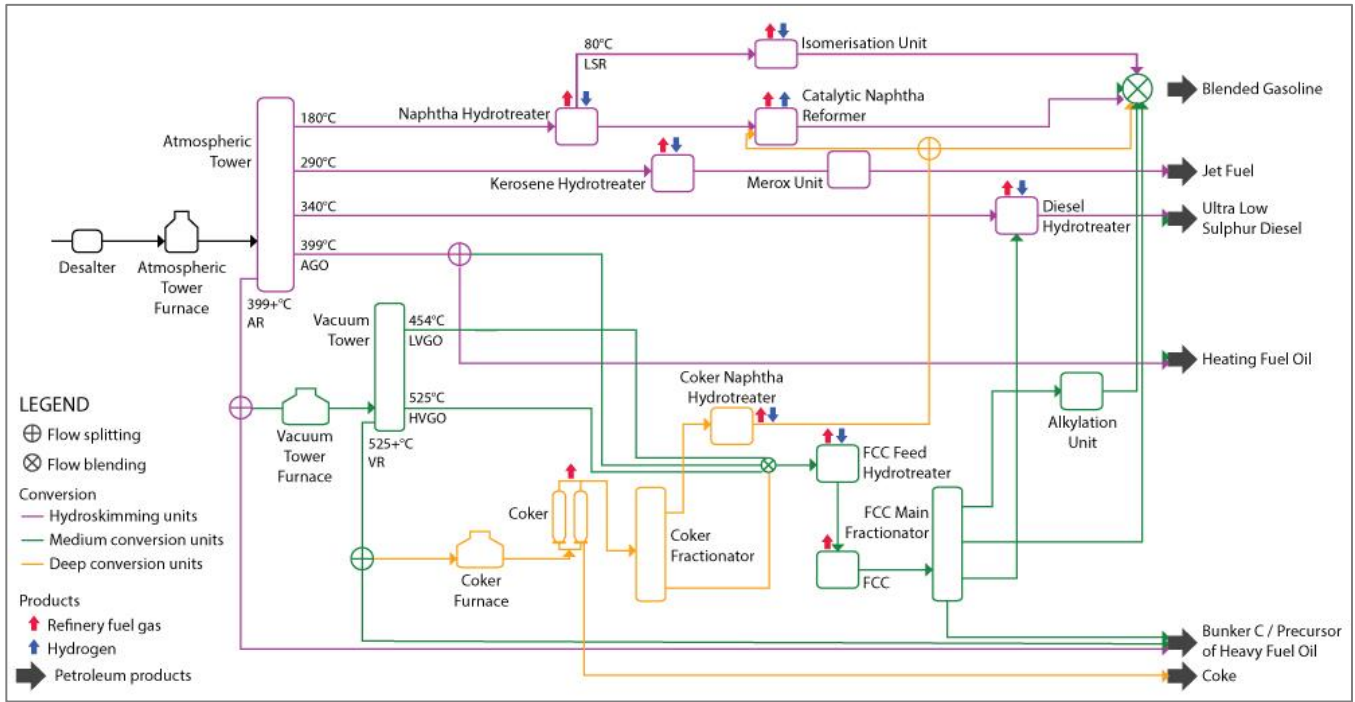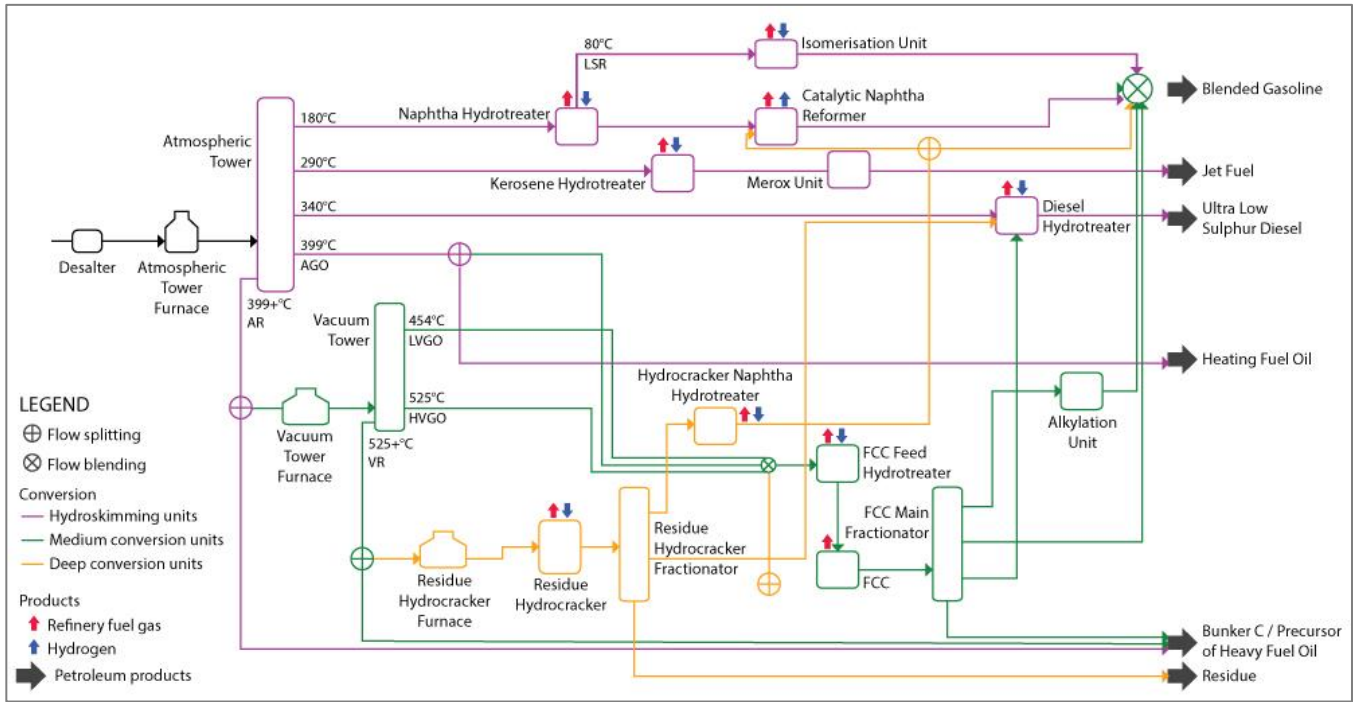
Figure 21: Configuration 7

In configuration 7, the hydroskimming process units, the process units associated with the fluid catalytic cracker (FCC), and the process units associated with the residue hydrocracker are enabled to provide a deep conversion.
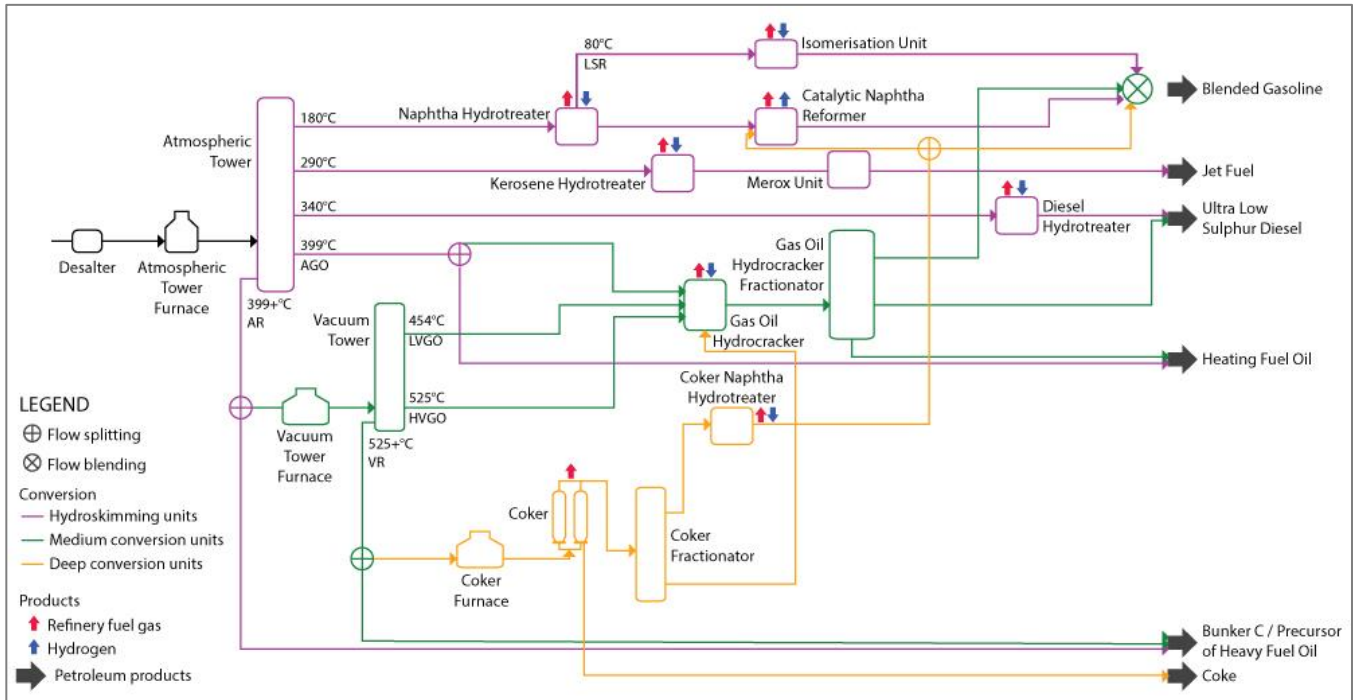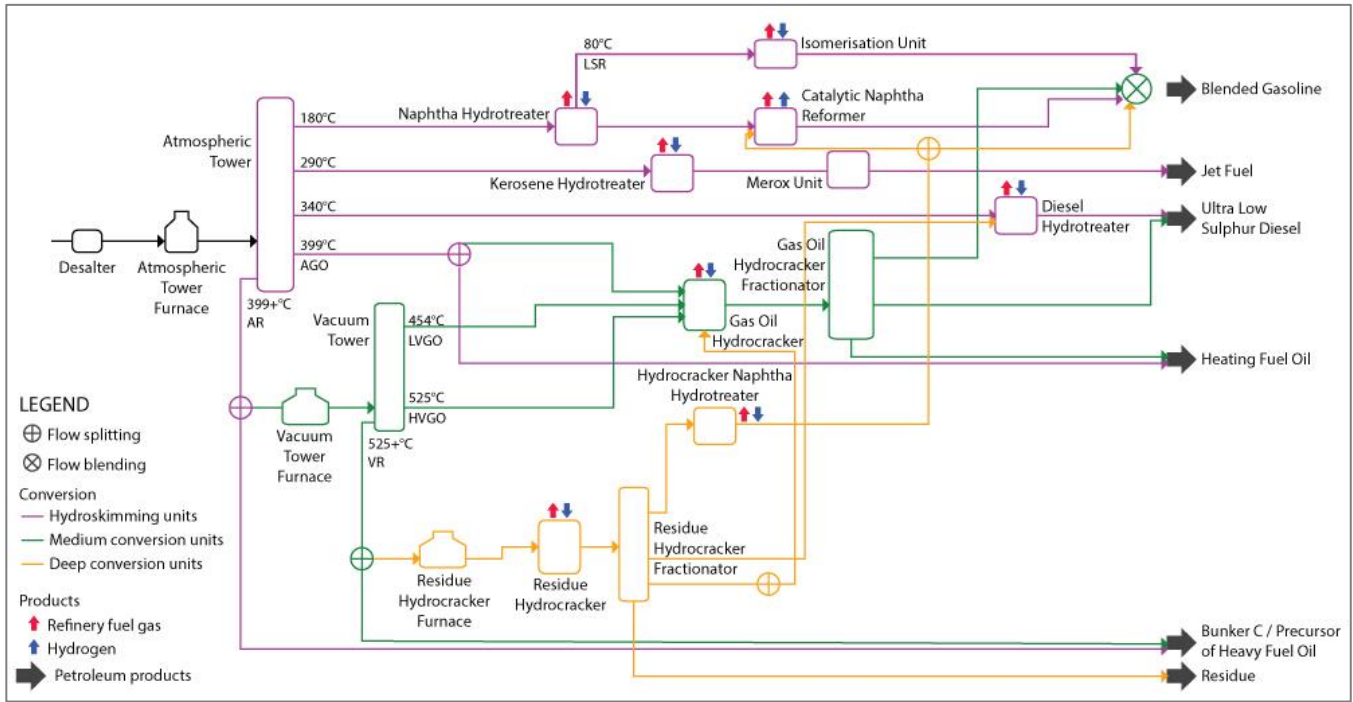
Figure 22: Configuration 8

In configuration 8, the hydroskimming process units, the process units associated with the gas oil hydrocracker, and the process units associated with the residue hydrocracker are enabled to provide a deep conversion.
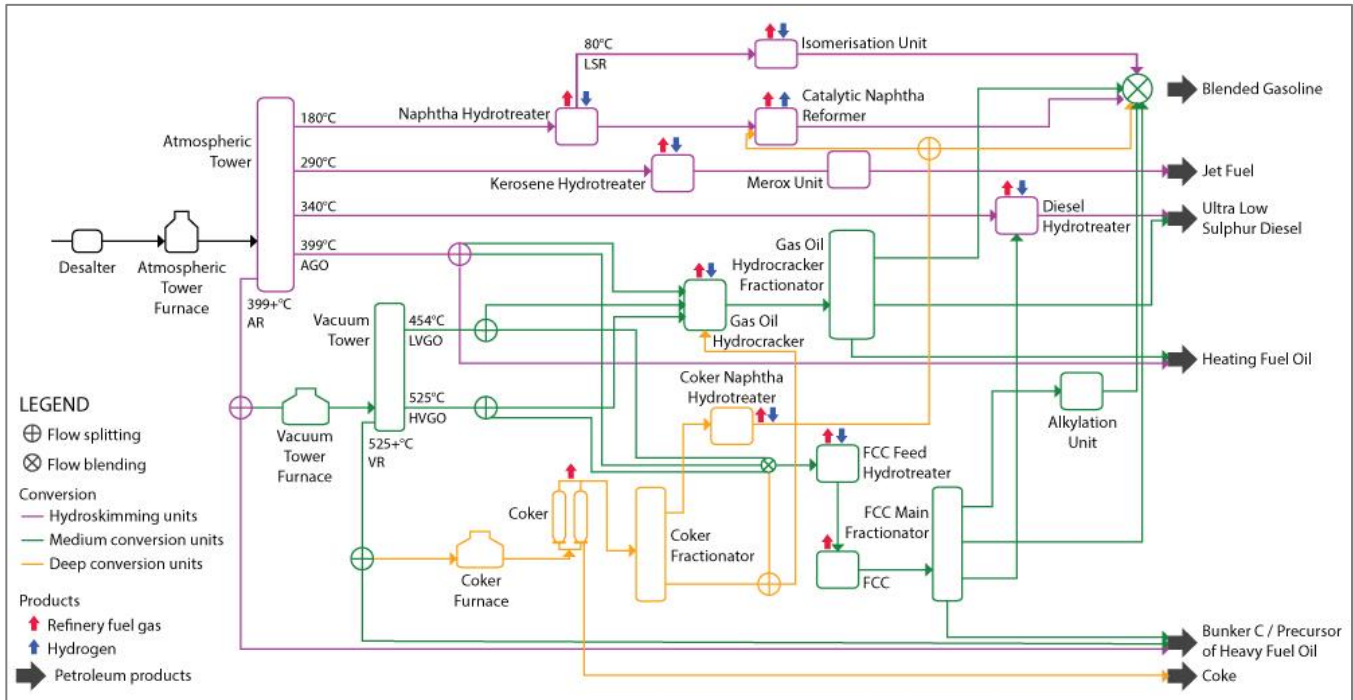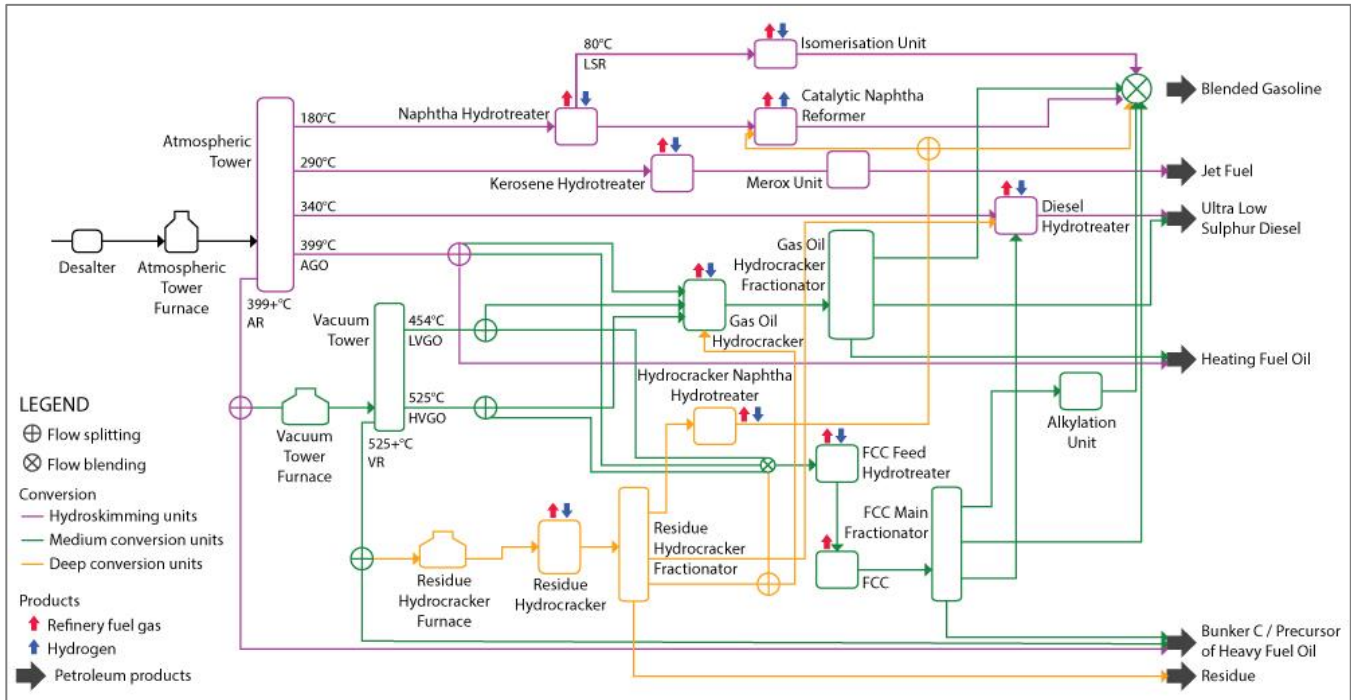
Figure 23: Configuration 9

> In configuration 9, the hydroskimming process units, the process units associated with the fluid catalytic cracker (FCC), the process units associated with the gas oil hydrocracker, and the process units associated with the residue hydrocracker are enabled to provide a deep conversion.

6.4.2 Process unit descriptions

The following process units are used in addition to the preceding ones when the hydrocracking deep conversion configuration is enabled.

> Note: PRELIM automatically chooses the default configuration to process crude oil using the method presented in Figure 5 as a default. However, the user can override the refinery configuration on the 'Main Inputs and Outputs' worksheet.

6.4.2.1 Residue hydrocracker furnace

6.4.2.1.1 Process unit description

Residue hydrocracker furnace preheats the input stream before it is processed in residue hydrocracker.

6.4.2.1.2 Input

Residue hydrocracker furnace is fed by a swing that distributes the vacuum residue (VR) coming from the vacuum tower.

6.4.2.1.3 Output

The preheated VR stream is sent to residue hydrocracker.

6.4.2.2 Residue hydrocracker

6.4.2.2.1 Process unit description

The residue hydrocracker unit breaks heavy petroleum fractions into simpler and lighter molecules, such as gasoline and kerosene, by the addition of hydrogen under high pressure in the presence of a catalyst. It increases the yield of lighter products from heavier fractions and primarily increases diesel yields.

6.4.2.2.2 Input

The VR stream comes from the residue hydrocracker furnace.

6.4.2.2.3 Output

The residue hydrocracker produces two streams:

- The processed stream is sent to the residue hydrocracker fractionator;
- Refinery fuel gas that can be reused within the refinery or sold as a product since it has properties close to natural gas.

The yield and product distribution calculations are based on the method proposed by Gary et al. (2007) and modified by input from industry experts.

6.4.2.2.4 Calculations

Correlation is based on feed Kw and approximated hydrogen consumption.

6.4.2.3 Residue hydrocracker fractionator

6.4.2.3.1 Process unit description

Residue hydrocracker fractionator separates the stream into four streams depending on the properties of the fractions.

6.4.2.3.2 Input

The input stream comes from residue hydrocracker.

6.4.2.3.3 Output

Residue hydrocracker fractionator produces four streams:

- The lightest stream (naphtha) is sent to hydrocracker naphtha hydrotreater for further processing;
- The second lightest stream is sent to diesel hydrotreater for further processing;
- The heavy stream (gas oil) is sent to a swing that distributes this stream to FCC feed hydrotreater and/or gas oil hydrocracker.
- The hydrocracking residue is not further processed and is sent to the residue pool.

6.4.2.4 Hydrocracker naphtha hydrotreater

6.4.2.4.1 Process unit description

Hydrocracker naphtha hydrotreater uses gas, electricity and hydrogen to reduce sulphur and nitrogen content, and to saturate olefins or aromatic rings of distillate fuels without changing the boiling range to meet specifications of stream for further processing, or specifications of end products (i.e. increase H/C ratio).

6.4.2.4.2 Input

The input stream consists of the light fraction coming from the top of residue hydrocracker fractionator.

6.4.2.4.3 Output

Hydrocracker naphtha hydrotreater produces two streams:

- The desulphurized stream is sent to a swing that delivers the stream to the naphtha catalytic reformer or directly to the gasoline pool depending on the selected `Naphtha catalytic reformer options` on the `Main Input & Output` worksheet. If `SR Naphtha` is selected, the output of the hydrocracker naphtha hydrotreater goes straight to the gasoline pool, and if `SR Naphtha + Heavy Naphtha` is selected, it is sent to the naphtha catalytic reformer;
- Refinery fuel gas that can be reused within the refinery or sold as a product since it has properties close to natural gas.

6.5 Other data and constants

6.5.1 Constants

The `Constants` worksheet provides all constants used in the calculation worksheets on a process unit basis. Each constant is presented with a unit, a minimum and a maximum value as well as a default value that can be overridden by advanced users. Some constants also include an average value, a median value, and a mode value.

This worksheet also includes the price of products used when the user selects the `Market Value Basis` as the allocation method.

> Source: product prices are obtained from historical North American data of Platts (www.platts.com), and CMAI (www.cmaiglobal.com).

6.5.2 Process correlations

The `Process Correlations` worksheet includes the calculations of yields and densities that are required for the hydrocracking and the fluid catalytic cracking process units. All correlations used in PRELIM are based on Gary et al. (2007).

6.5.3 Energy & Unit Conversions

The `Energy & Unit Conversions` worksheet gathers all factors used to convert values in imperial units into metric units, and vice versa.

6.5.4 Emissions factors

The `Emissions Factors` worksheet includes the greenhouse gas emission factors associated with each process unit.

6.5.5 TRACI CFs

The `TRACI CFs` worksheet includes characterization factors for calculating life cycle impacts related to global warming, acidification, particulate matter, eutrophication, ozone depletion, smog, human health (cancer), human health (non-cancer), and ecotoxicity.

6.5.6 Assay inventory

The `Assay Inventory` worksheet displays all the crude oil assays available in PRELIM. It also displays the `Custom Assay` that a user can input on the `Expert Inputs` worksheet as well as the assay resulting from the `Crude Blender` tool at the bottom of the worksheet.

The crude oil assays presented in this inventory have been selected in attempt to provide examples of the range in quality of crudes produced and used globally. This also helps to show a range of possible energy requirements associated with this varying quality. However, they are not exhaustive, and this inventory will be expanded further in future versions of PRELIM.

This worksheet should not be modified as it is used by the macros used to blend crude assays.

6.6 OpenLCA input sheets

6.6.1 General Information

The `General information` worksheet provides some basic details about refinery configuration, allocation method, as well as quantitative references, time, geography, and technology used in PRELIM (e.g., electricity source, SMR hydrogen purification method).

6.6.2 Inputs

The `Inputs` worksheet includes all PRELIM inflows and elementary inflows based on a 1 kg crude oil input functional unit. The first flow "crude oil, at refinery" summarizes the name and density of the crude oil assay selected for evaluation. Crude oil mass flow is also set to 1 kg such that all other flows are adjusted to match. Electricity and natural gas flows are all 0 if the user chooses to include the upstream emissions in the `Main Input & Output` worksheet as these emissions are already included in the inventory. Water consumption is divided into river (72% pre-set), well in ground (10% pre-set) and unspecified origin (18% pre-set). Catalysts, acids, and land use is also included.

6.6.3 Outputs

The `Outputs` worksheet includes all refinery products shown in the `Main Input & Output` worksheet and all by-products based on 1 kg crude oil input.

6.6.4 Allocation

The `Allocation` worksheet allocates all flows contained in the `Inputs` and `Outputs` worksheets to all refinery products from gasoline to asphalt depending on which products are selected for allocation in the input section of the worksheet.

Part III Model evaluation

Since PRELIM attempts to balance the ease of use and simplicity that informs policy analysis with the rigor required to produce reliable estimates, it is imperative that all methods, data, and results be evaluated against more detailed refinery models. This section presents the methods employed for such evaluations. In particular, this section describes the approach used to assess the proximity of PRELIM estimates to a more complex proprietary refinery model and presents a comparison of PRELIM against other model estimates for overall refinery CO_2 emissions, product yields, process energy requirements, and hydrogen requirements. In addition, PRELIM results from using the assay transformation method described in section 5.4.1 are compared to those from using the assay data from a more comprehensive proprietary database. Finally, a comparative analysis of the implications of enhancements made in the current version of PRELIM is made versus initial version of the model (2012) and within the model itself.

Detailed findings are discussed throughout. It should be noted although these evaluations were done for earlier versions of PRELIM (e.g., PRELIM v1.2), these findings are still valid for the latest PRELIM v1.3.

7 Methods for model evaluation

PRELIM reduces the level of complexity in modelling refinery operations from the models used by industry to optimize their operations (See Parkash [2003] for a detailed description about refinery linear programming modelling). Confidential data (associated with crude assays, operating conditions, and energy estimates) and discussion with refining experts are necessary to assess the validity of PRELIM input data and assumptions. In addition, sensitivity analyses and/or alternative logic calculations to estimate hydrogen content of intermediate products, API of the heaviest fractions, and the Kw parameter need to be conducted. There is also a need to evaluate PRELIM outputs against those of a more detailed refinery model in order to assess its performance, identify any improvements required, and to specify the level of accuracy that can be expected when using the model to inform policy (referred to hereafter as the co-validation process).

Two industry standard tools are used, with input from industry experts, to co-validate two key aspects of PRELIM: 1) a detailed but generic proprietary refinery linear programming model (PRISM^{TM}) is used for estimates of refinery energy requirements and product yields based on PRISM^{TM} (Baker & O'Brien PRISM Overview, http://www.bakerobrien.com/services/PRISM) assumptions for a specific crude assay. PRISM^{TM} is a good basis of comparison as it focuses on very detailed energy requirements and product yield calculations (e.g., PRISM^{TM} uses alternative calculation methods which include operating conditions as modelling parameters in some process units) whereas PRELIM focuses on detailed GHG emissions estimates. 2) Haverly's Crude Assay Management System (H/CAMS) is used to evaluate the transformation of public assay data into data used as input to the current PRELIM crude assay inventory (Haverly Systems Inc. Haverly's Crude Assay Management System, http://www.haverly.com/main-products/13-products/10-hcams). H/CAMS includes a comprehensive proprietary assay database and applications that allow the prediction of cut yields and properties for single or blends of crudes (Haverly Systems Inc.). The accuracy of these tools is accepted by industry, and they are commonly used for the analysis of industrial operations and business planning. Permission to use these tools for PRELIM evaluation was obtained and published in Abella (2012).

This model validation was conducted when the model was first published in the academic literature in 2012. At that time, PRELIM's crude assay inventory included publicly available assay data that represented 22 Western Canadian Basin crudes tracked by the Canadian Crude Quality Monitoring Program (CCQMP). Small changes were made to the model since its first version; however, the comparisons made during the validation are still valid.

7.1 Co-validation for estimates of refinery energy requirements and product yields

A total of 22 runs in PRISM^{TM} are used for the assessment of refinery energy requirements and product yields. Three out of the 10 PRELIM configurations were replicated in PRISM^{TM}. One is the hydroskimming configuration suitable to process only light sweet crudes, and the other two are deep conversion configurations that can be applied to refining any crude: (1) delayed coking and FCC process units present, and (2) delayed coking, FCC, and gas oil hydrocracking process units present. Also, ten crudes of different quality are selected to be run in both PRISM^{TM} and PRELIM, including a light sweet conventional crude and a light sweet SCO. These crude assays also include oil sand products – bitumen, dilbit, syndilbit, synbit, heavy SCO – and Canadian conventional crudes – light sour, medium, and heavy. H/CAMS assay information is selected to be used over PRELIM crude assay inventory to decouple differences between the model outputs due to differences in the crude assay information and due to differences in modelling approaches. Similarly, in order to obtain comparable results, PRELIM assumptions about process energy requirements (which included steam exports from naphtha catalytic reforming, delayed coking,

and FCC process units), and emission factors for natural gas (combustion, no upstream emissions) and electricity are set equal to the corresponding assumptions in PRISM™. Common outputs of the model such as refinery final product yields (i.e. gasoline, diesel, fuel gas and coke) and energy requirements (i.e. FCC coke-burned, on site produced gas, natural gas, electricity, and hydrogen requirements) as well as refinery CO_2 emissions are compared to assess overall proximity between model results.

Because PRISM™ does very detailed energy requirement and product yield calculations using methods that are different from PRELIM, it is used as the basis to mathematically measure how well the models (PRISM™ and PRELIM) outputs match (proximity criteria). Three measurements are employed as described here:

1) Coefficient of Variation of the Root-Mean-Square Deviation (CV (RMSD)) to quantify the magnitude of under or overestimates specific to an output. In this case, it calculates the square root of the variance between PRISM™ and PRELIM estimates for a crude, normalized by the mean of the PRISM™ estimates:

$$CVRMSD\left(\theta_{PRISM^{TM}}, \theta_{PRELIM}\right) = \frac{\sqrt{\frac{\Sigma_{i=1}^{n}\left(x_{PRISM^{TM},i} - x_{PRELIM,i}\right)^2}{n}}}{\overline{X_{PRISM^{TM}}}} \times 100\%; \quad \theta = \begin{bmatrix} x_1 \\ \vdots \\ x_n \end{bmatrix}$$

Where:

$\theta = Model\ output\ such\ as\ MJ\ of\ electricity\ required\ per\ MJ\ of\ crude\ being\ processed$

$x = value\ estimated\ by\ a\ model\ in\ a\ run\ for\ a\ particular\ output$

$n = number\ of\ runs = 22$

$\overline{X_{PRISM^{TM}}} = average\ of\ values\ estimated\ by\ PRISM^{TM}$

$Numerator\ provides\ the\ variance\ between\ model\ outputs\ in\ the\ same\ units\ (e.g., MJ)$

$Denominator\ provides\ an\ estimate\ of\ the\ variance\ expresed\ as\ a\ percentage$

For example, over all runs and configurations, the deviation in CO_2 emissions between PRISM™ and PRELIM is estimated to be 0.7 g CO2/MJ of crude, or 10% relative to PRISM™ estimates. Under or overestimates are illustrated by using scatter diagrams where the x-axis is used to represent PRISM™ estimates and the y-axis is used to represent PRELIM estimates. Data points over the diagonal line indicate where PRELIM overestimates, whereas data points under the diagonal line illustrate that PRELIM underestimates.

2) The coefficient of determination (r^2) to quantify proximity to reproduce variability in model outputs due to crude assay information ("natural" variability due to crude quality). In this case, it calculates the squared value of the coefficient of correlation or the combined variation against the single variation of the PRISM™ estimates and PRELIM estimates for a particular model output:

$$r^2 = \left(\frac{\sum_{i=1}^{n}\left(x_{PRISM,i} - \overline{X_{PRISM}}\right)\left(x_{PRELIM,i} - \overline{X_{PRELIM}}\right)}{\sqrt{\sum_{i=1}^{n}\left(x_{PRISM,i} - \overline{X_{PRISM}}\right)^2}\sqrt{\sum_{i=1}^{n}\left(x_{PRELIM,i} - \overline{X_{PRELIM}}\right)^2}}\right)^2$$

Where:

$x = value\ estimated\ by\ a\ model\ in\ a\ run\ for\ a\ particular\ output\ (e.g., electricity)$

$\bar{X} = average\ of\ \ values\ estimated\ by\ a\ model$

$n = number\ of\ runs = 22$

The r² value describes how much of the variation in PRISM™ estimates is represented by the variation in PRELIM estimates. The r² value may range from 0 to 1. A value of 0 represents no correlation while a value of 1 represents that the variation is similar in the estimates from both models. In other words, a r² close to 1 indicates that PRELIM is able to reproduce the "natural" variability in model outputs (associated with a particular crude and configuration) predicted by PRISM™ very well (Krause et al., 2005).

3) A weighted coefficient of determination (wr²) to measure the "overall model match". This coefficient is an indicator that combines the model performance in reproducing the variability specific to an output/estimate as indicated above, measured by the coefficient of determination, and the magnitude of under- or over-estimates using the gradient of correlation (i.e., the slope of the regression on which r² is based. If the equation of a line is expressed as y = bx + c; the gradient of correlation (b) should be close to 1 if there is good agreement between the two estimates. If the intercept of the regression (c) is 0, the gradient of correlation indicates the magnitude of the under or overestimates. For example, in a scatter diagram in which the x-axis is used to represent PRISM™ estimates and the y-axis is used to represent PRELIM estimates, a gradient of linear regression of 0.5 means that PRELIM underestimates PRISM™ outputs by 50% if the intercept is 0. In this application, the intercept may not be 0, and therefore, the gradient of correlation is not used to indicate the magnitude of under or over estimates. The CV (RMSD) is used for this purpose as explained above. However, the weighted coefficient of determination is still meaningful to quantify the overall model match as it is based on the principles of least squares. The weighted coefficient of determination (wr²) is proposed in Krause et al. (2005) to be calculated as follows:

$$wr^2 = \left\{ \begin{array}{l} |b| \ \times \ r^2 \ for \ b \leq 1 \\ |b|^{-1} \ \times \ r^2 \ for \ b > 1 \end{array} \right\}$$

Where:

$b = slope\ or\ regression\ coefficient\ \ resulting\ from\ linear\ regression$

$between\ PRISM^{TM} and\ PRELIM\ estimated\ values\ for\ a\ particular\ output$

The range of values for wr² is from 0 to 1; where a value of 0 means no proximity while a value of 1 means a perfect "match". Therefore, "overall model match" can be ranked based on the wr² value. The following rank was used to characterize the match between PRISM™ and PRELIM estimates: Low match (wr² < 0.5) intermediate match (0.5 < wr² < 0.7), high intermediate match (0.7 < wr² < 0.9), and high (0.9 < wr²). wr² values are also reported.

7.2   Co-validation for transformation of publicly available assay data in PRELIM

The quality of crude assay data is evaluated by measuring how variations of assay information can affect the modeling precision of PRELIM in GHG estimates. There are 99 runs in PRELIM for such assessment by using both H/CAMS assays and PRELIM crude assay inventory data. Nine out of the 10 crude assays selected for co-validation are studied; the 10th is excluded based on completely dissimilar whole crude characteristics such as sulphur, API,

and distillation curve between the H/CAMS and PRELIM assay data implying that the crudes considered were significantly different. Also, each crude is run in nine configurations, and in one configuration at two levels of energy use (a total of 11 refinery cases). Overall refinery GHG emissions as well as GHG emissions allocated to gasoline and diesel are tabulated for the analysis (allocation only to transportation fuels is used). Measurement of the variation in PRELIM GHG estimates for each crude as well as the deviation in each individual quality parameter is used to gain information about quality of the PRELIM assay data, limitations of the transformation methods adopted, and needs for improvement of assay data. The Coefficient of Variation of the Root-Mean-Square Deviation (CV (RMSD)) is used to quantify the magnitude of the variance in PRELIM GHG estimates; the square root of the variance is normalized by the mean of PRELIM estimates when H/CAMS assay data are used.

7.3   Validation of gasoline Reid Vapor Pressure
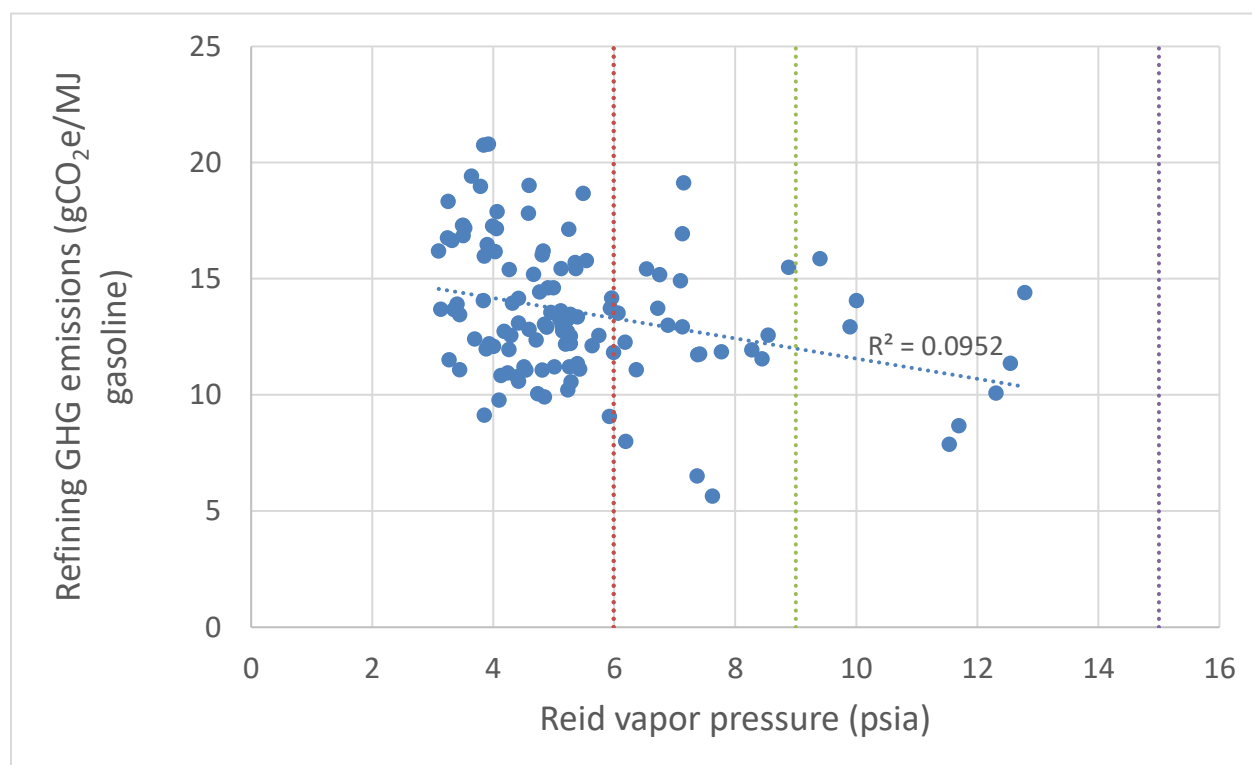
Of the 113 assays in the PRELIM v1.2 inventory, 74% of assays, when run in a deep conversion configuration, produced a final gasoline product below 5.99 psia RVP (this drops to 65% for the medium conversion configuration where there is less low-RVP gasoline blendstock produced from the heavier fractions). A small fraction of assays (11% and 7% for medium conversion and deep conversion, respectively) produce a final gasoline product above 9 psia RVP (the summer minimum in most US states). While most of these assays are ultra light or condensates (characterized by very high API gravity), assays with low API (e.g. Synbit Blend) can also produce a high RVP gasoline if they have a significantly large light straight run fraction with a sufficiently low boiling point. Also, not all ultra light assays produced a high RVP product (e.g. Eagle Ford Ultra Light produced a 6.36 psia RVP gasoline). Emissions allocated to gasoline among these high RVP assays also varied drastically, from 7.9 to 16 gCO2e/MJ gasoline.

The linear regression through these points suggests an inverse relationship between emissions allocated to gasoline and RVP – however, the coefficient of determination (r^2) of 0.0952 is quite low, suggesting weak

correlation. Due to the large range of emissions which exists for any RVP value, it seems inconclusive to link GHG emissions to RVP without examining other properties of the crude. Grouping the crudes into bins based on API gravity or percentage of light straight run naphtha (LSR) in the assay does not seem to provide any better correlations. It does appear that higher API crudes generally have lower GHG emissions per MJ of gasoline, due to the relatively low energy required to process lighter fractions. Crudes with larger LSR fractions generally have a higher RVP, due to typically high RVP values of isomerate. As such, it seems sensible for refiners to blend crudes that have large LSR fractions with crudes that have small LSR fractions when looking to meet RVP specifications.

8   Comparison of fit between PRISM™ and PRELIM

PRELIM can estimate the energy use and GHG emissions associated with a crude in different configurations (as more complex refinery models do) with a margin of error appropriate between the bounds of life cycle analysis and the transparency needed to inform policy. This section presents the results of the co-validation process that measures the difference between estimates of the two models. This process helps to highlight the difficulty in replicating estimates not only due to differences in modelling approaches but also due to the level of complexity and flexibility that exists in operating processes in refineries.

8.1   Overall model performance

Overall refinery emissions estimates are used as the first level of comparison of the models. These emissions estimates include CO_2 emissions that result from gas combustion, SMR emissions, FCC coke-burned, and indirect emissions due to electricity use. Figure 24a shows the refinery emissions estimates (g CO_2/MJ of crude) for a range of crudes with PRELIM results on the y axis and PRISM™ results on the x axis. Figure 24b and Figure 24c show the same plot but with functional units of per MJ of gasoline and per MJ of diesel, respectively (no allocation procedure is applied in PRELIM [see section 4] to be consistent with PRISM™).

It is illustrated that there is a good agreement (match) between two models' estimates. PRELIM replicates 93% of the variability in CO_2 emissions due to crude quality and configuration, and the deviation calculated as a Coefficient of Variation of the Root-Mean-Square Deviation is low (CV(RMSD) 10%). The deviation in the estimates is considered appropriate within the bounds of life cycle assessment. More generally, literature in the field of life cycle assessment suggests that standard deviations for variation in emissions range from a typical 20% (when assessing existing technologies and processes) up to 100% for estimating less certain technologies (e.g., emerging technologies and processes [Lloyd et al., 2007]).
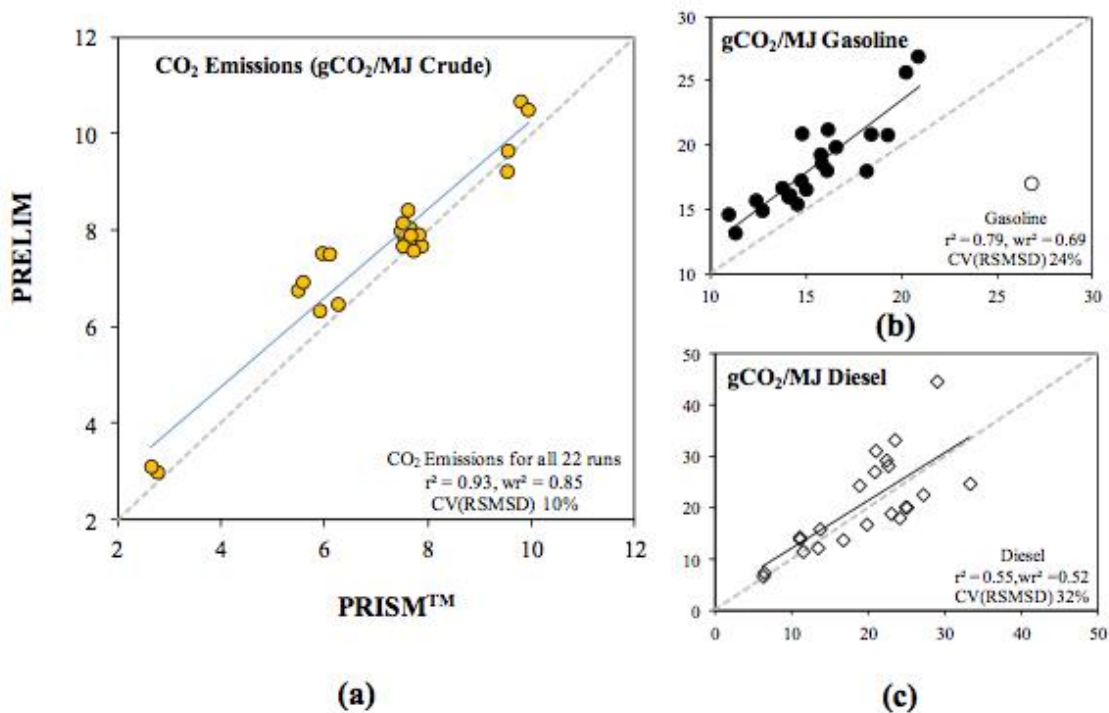
Figure 24: Comparison of Fit between PRISM^{TM} and PRELIM CO$_2$ Estimates

The x-axis shows PRISM^{TM}'s CO$_2$ emissions (g CO$_2$/MJ Crude), and the y-axis shows PRELIM's CO$_2$ emissions (g CO$_2$/MJ Crude). Solid lines illustrate deviations that are due to variation in crude properties.

It includes onsite emissions from gas combustion, hydrogen production via steam methane reforming, and indirect emissions due to electricity use. r^2: coefficient of determination, wr^2: weighted coefficient of determination accounting for gradient of correlation to quantify overestimates and variability together. CV(RSMSD): coefficient of variation of the root-mean-square deviation (normalized by the mean of PRISM^{TM} estimates). Diagonal dotted lines illustrate deviations that are due to variation in crude properties.

There are methodological compromises when the unit of measurement changes from the overall refinery basis (i.e., g CO$_2$/MJ Crude) to a per MJ product basis. The match rank goes from a high to an intermediate value and the estimate deviation increases. However, such behaviour is more of a reflection of possible operating conditions (e.g., temperature and pressure) and configurations being modelled rather than one model being more accurate than the other. Further details are discussed in the following sections, which demonstrate that no simple calibration process can be followed to match the models' performance if the flexibility and variability that exist in real refinery operations is considered. This demonstrates the value of having a simple and flexible tool. Nonetheless, the comparison of these models helps raise questions about potential improvements in PRELIM to model the refinery system. Despite using the same assumptions in both models, uncertainty may come from the modeling structures and data sources. To explore the source of the variability observed between the models, intermediate model estimates or outcomes are explored in the following.

8.2   Product yields

One key element in comparing the models is the amount of each final product produced from processing a certain crude. Therefore, it is important to compare the amounts of refinery final products (e.g., gasoline and diesel) obtained from a specific crude in a configuration. Figure 25 shows the models' estimates of product yields for gasoline and diesel (MJ of product/MJ of crude processed) for the same set of crudes grouped by configuration. The comparison of the models' estimates of product yields demonstrates several points: a) the assessment of overall emissions on a per MJ product basis is impacted by the type of configuration being modelled, b) PRELIM can replicate the "natural variability" in model outputs predicted by PRISM^{TM} due to the quality of the crude in a specific refinery configuration, c) the magnitude of the deviations in final product yields are mainly associated with deviations resulting from modelling the hydrocracking process unit, d) deviations may also result from the different level of detail in modelling process unit operating conditions between the two models or divergence in the accuracy in the process unit product yield correlations.

The assessment of overall emissions on a per MJ product basis is impacted by the type of configuration being modelled. In Figure 24b and Figure 24c, agreement between the models' overall emissions estimates on a per MJ product basis (i.e., overall emissions divided by the final product yield) are evaluated over all of the runs regardless of the configuration that is modelled. Figure 25 also helps to illustrate that the configuration plays an important role in the assessment of the magnitude of variability and deviations.

Figure 25: Comparison of fit between PRISM™ and PRELIM final product yields estimates

The x-axis shows PRISM™'s final product yields (MJ/MJ Crude), and the y-axis shows PRELIM's final product yields (MJ/MJ Crude). Solid lines illustrate deviations that are due to variation in crude properties.
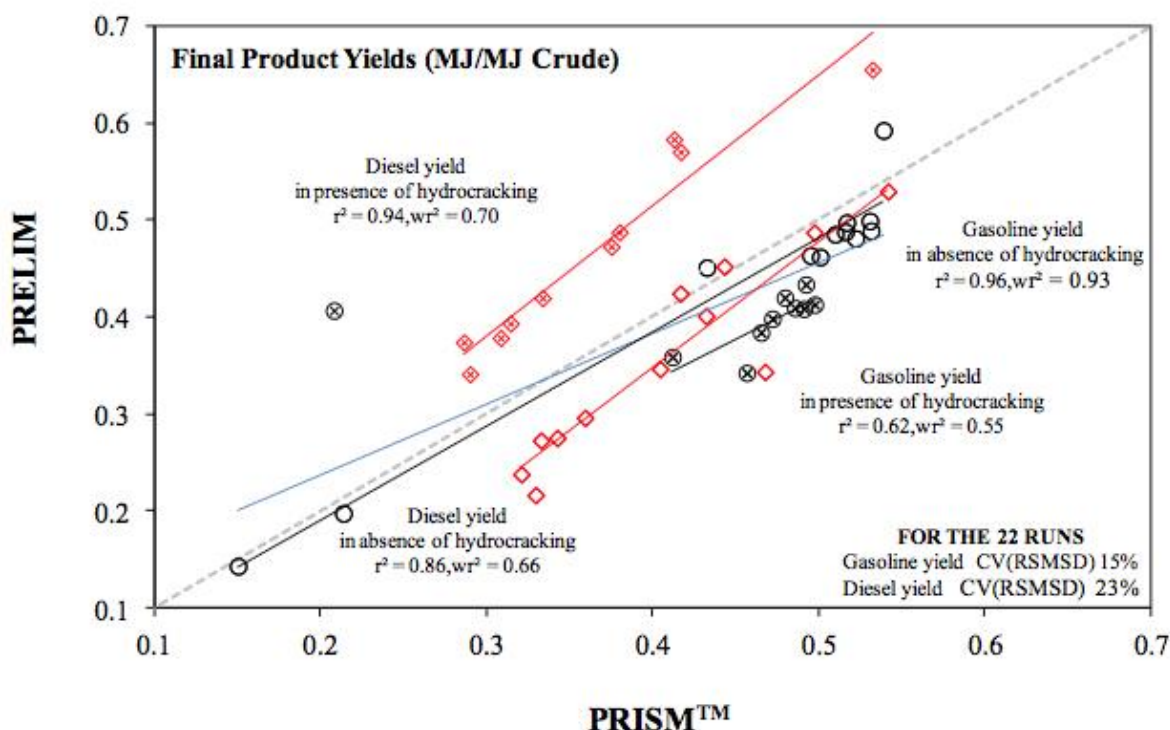
White series denotes: Gasoline and diesel productions in hydroskimming configuration or configuration where delayed coking and fluid catalytic cracking are present (in absence of hydrocracking). X series denotes: Gasoline and diesel productions in configuration where delayed coking, fluid catalytic cracking, and gas oil hydrocracking are present (in presence of hydrocracking). r^2: coefficient of determination, wr^2: weighted coefficient of determination accounting for gradient of correlation to quantify overestimates and variability together. CV(RSMSD): coefficient of variation of the root-mean-square deviation (normalized by the mean of PRISM™ estimates).

Once there is an agreement on the type of refinery processes to include, Figure 25 shows that PRELIM can replicate the "natural variability" in model outputs predicted by PRISM™ due to the quality of the crude. PRELIM can replicate most of the variability in gasoline and diesel yields in hydroskimming and deep conversion configurations, without a gas oil hydrocracking process unit (r^2=0.95 for gasoline; r^2=0.86 for diesel). Also, in the presence of hydrocracking, there is an acceptable and good replication of variability in gasoline and diesel yields respectively (r^2=0.62 for gasoline; r^2=0.94 for diesel). If overall refinery emission estimates on a per MJ product basis are analyzed in this way, it shows that PRELIM can replicate most of the variability of PRISM™ estimates as well. The coefficient of determination that represents how much of the variation in PRISM™ estimates is represented by

the variation in PRELIM estimates improves from the aggregated coefficient of determination presented in Figure 24 for both products and the three configurations (Figure 25 shows that r^2 improves to a value of 0.85 for gasoline and to 0.97 for diesel). Therefore, PRELIM is reliable in capturing and demonstrating the variability of emissions estimates originating from processing different crudes in different configurations.

Also, Figure 25 illustrates that the magnitude of the deviations in final product yields (therefore in overall emissions on a per product basis) are mainly associated with deviations resulting from modelling the hydrocracking process unit. It is difficult to determine the exact source of the deviation considering the flexibility in operating conditions that exists for this specific process unit. The hydrocracking process unit can be used to produce more gasoline or more diesel depending on process operating conditions. At first glance, it seems that the PRELIM hydrocracking product yield correlations favours diesel production. When the hydrocracking process unit is not present, PRELIM underestimates diesel yields (i.e., Figure 25 shows that the data points associated with diesel production in absence of hydrocracking are under the diagonal dotted line). However, PRELIM hydrocracking product yield correlations should favour gasoline production (Gary et al., 2007), which is consistent with the basic modelling option that is selected in PRISM^{TM} for the purposes of the co-validation. This suggests that PRISM^{TM} may model more severe operating conditions that increase gasoline yield at the expense of reducing diesel yield. For the purposes of co-validation, PRISM^{TM} is run at a 70% level of conversion of process unit feed to lighter products. In real operations, in a highly efficient hydrocracking process unit, conversion could range from 50 to 70% (Gary et al., 2007). Therefore, correlations used in PRELIM are plausible and likely represent a process unit with less efficient conversion.

On the other hand, Figure 25 indicates that deviations may also result from the different levels of details in modelling process unit operating conditions between the two models. It is not clear if PRISM^{TM}'s capability to account for process unit operating conditions such as pressure or temperature could be internally used by PRISM^{TM} to determine product yields specific to each crude. For example, PRELIM's estimates of coke yield from the delayed coking unit are consistently higher than PRISM^{TM} estimates for all crudes whose crude quality is below the quality of a conventional light sour crude in opposition to coke yield from the sweet light crudes (coke yield 40% CV(RSMSD)). Operating conditions in the delayed coking process unit do change coke yields. An increase in coke yield can result in consistently underestimating both gasoline and diesel yields when the hydrocracking process is absent (Figure 25). Another example is the outlier in Figure 25 for gasoline yield (when the hydrocracking process unit is present). It corresponds not only to the conventional light sweet crude, but also to a case where refinery final gasoline yield is influenced by changes in the extent of hydrocracking (i.e., amount of hydrogen added). Because PRISM^{TM} is consistently run at a 70% conversion rate, it could represent a low extent of hydrocracking for this crude that is easy to be processed. On the other hand, PRELIM is consistently run assuming the same level of hydrocracking (approximately 1,500 standard cubic feet of hydrogen per barrel of feed) to process all crudes; a more intense level of hydrocracking compared to the level that PRISM^{TM} could have assumed for this crude. It is possible to run PRELIM at a level of hydrocracking to be comparable to PRISM^{TM}; however, a relationship between conversion (input parameter in PRISM^{TM}) and approximate hydrogen requirement (input parameter in PRELIM) need to be determined. Therefore, PRELIM appears to overestimate gasoline production specific to this crude as opposed to the underestimates of other crudes. When PRELIM is run with decreased level of hydrocracking (e.g., change from adding 1,500 to 500 standard cubic feet of hydrogen per barrel of feed), the refinery gasoline yield estimated for this crude is reduced by 12%. Same as the delayed coking process unit, it is unknown how PRISM^{TM} internally models and links variables such as the extent of hydrocracking to feed quality.

Moreover, the condition of over or underestimating final product yields as well as the magnitude of the deviations partially results from divergence in the accuracy in the process unit product yield correlations. Like PRELIM, PRISM™ correlations have been derived from a set of process unit operating conditions, including a set of crude runs, and it is unknown to what extent the correlations in both models can be generalized to all crude of different quality. This includes the crudes derived from bitumen (crude of largest deviation in final product yield estimates). Both, PRELIM and PRISM™ correlations could be correct with some margin of error (difficult to determine), and therefore their process yields are likely to be equally valid but different with some uncertainty inherent to the modelling process.

Considering the points above, over all the runs, PRELIM deviations in gasoline and diesel yield are acceptable (15% and 23% CV(RSMSD) respectively) and can be explained by differences in model approaches. The overall model match on these outputs ranks at a high intermediate and intermediate value (average wr^2=0.74 on gasoline yield; average wr^2=0.68 on diesel yield) and is mostly affected by process unit operating conditions that could be modelled by establishing a clear link between them and the feedstock quality as further development of PRELIM.

8.3   Gas requirement

The proximity of the models in estimating the gas required by the refinery to process a crude is presented in Figure 26. Gas requirement is the single most important process energy requirement in refining crude oil. It is used to supply heat, steam, and hydrogen. PRELIM and PRISM™ estimates show that on an energy basis, gas requirement estimates are up to ten times higher than those for electricity and five times higher than those for FCC coke burned. Estimates of the gas requirement will affect how much gas is purchased from offsite and CO_2 emissions associated with gas combustion as well as the chemical transformation of gas into SMR hydrogen. Also, gas requirement affects the upstream impacts of purchased gas via production, processing, and transport.

Figure 26 shows the comparison of gas requirement estimates from both models in terms of total energy requirement as well as energy required from offsite. The comparison implicitly compares the models' proximity in three outputs: 1) match in gas requirement due to hydrogen demand, 2) proximity in gas requirement due to process energy requirements, and 3) match in onsite fuel gas production estimates. The latter compares two different levels of aggregation by modelling the amount and quality of the fuel gas. Conversely to PRISM™, PRELIM calculation method groups lighter gases; i.e. they do not distinguish between methane, ethane, propane, and butanes, and generalize fuel gas production yields in all hydrotreating process units.
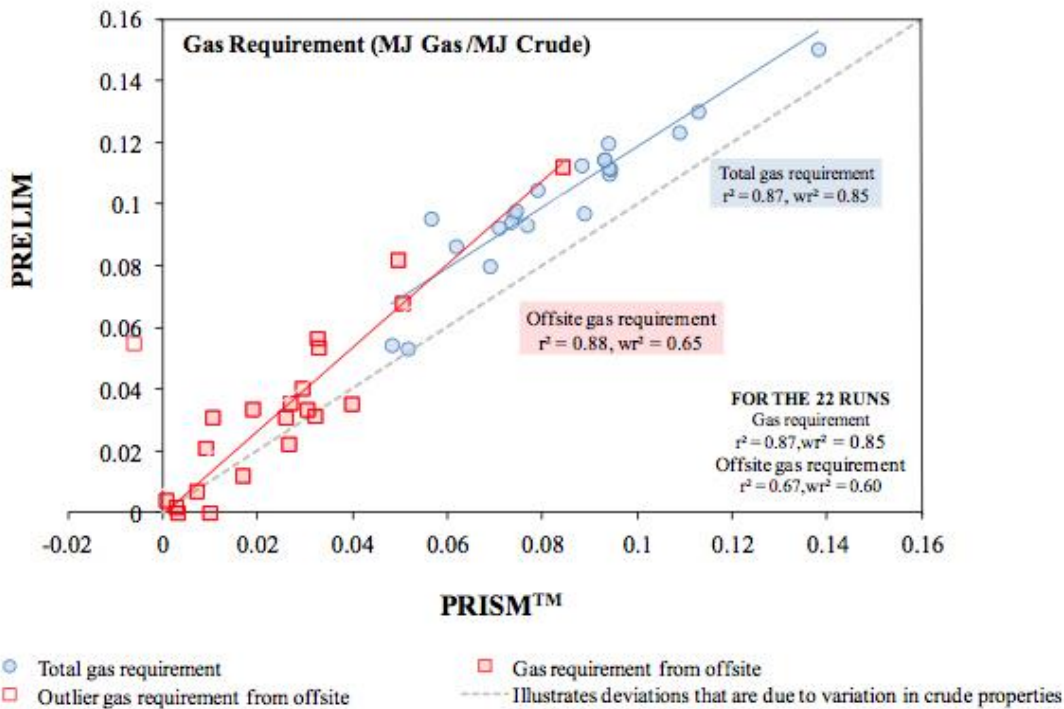
Figure 26: Comparison of Fit between PRISM^{TM} and PRELIM Gas Requirement Estimates

The x-axis shows PRISM^{TM}'s gas requirement (MJ Gas/MJ Crude), and the y-axis shows PRELIM's gas requirement (MJ Gas/MJ Crude). Solid lines illustrate deviations that are due to variation in crude properties.

Total gas requirement includes gas associated with heating, steam, and chemical transformation hydrogen via steam methane reforming. Gas requirement from offsite equals total gas requirement minus gas produced onsite; PRISM^{TM} estimates of propane produced are included. Outlier: light sweet synthetic crude oil assay run in configuration where delayed coking and fluid catalytic cracking are present. r^2: coefficient of determination, wr^2: weighted coefficient of determination accounting for gradient of correlation to quantify overestimates and variability together.

Figure 26 shows that PRELIM replicates most of the "natural variability" in total gas requirement and offsite gas requirement for various refinery configurations and types of crude. PRELIM reproduces similar variability of gas requirement for all 22 cases (r^2=0.87 gas requirement). Also, PRELIM replicates the variability in offsite gas requirement for most of the runs (r^2=0.88 offsite gas requirement for 19 out of 22 runs). In addition, Figure 26 illustrates that PRELIM's estimates of gas requirements are consistently high. Such deviation (24% CV(RSMSD) is considered acceptable as it results from the combined effect of several factors and does not end in a large deviation in the overall refinery emission estimates (total gas requirements match ranks at a high intermediate value; wr^2=0.85). Differences in modelling hydrogen requirements (section 8.4) only partially explains the deviation in total gas requirements. For example, excluding the models' gas requirement estimates associated with hydrogen requirements, the deviation in total fuel gas requirement increases (35% CV(RSMSD) indicating a cumulative impact of other factors such as differences in process unit product yields that reflect the range of operating conditions possible (section 8.2). Besides that, the significant deviation in offsite gas requirements (46% CV(RSMSD) is considered acceptable for PRELIM because it does not have any significant impacts on emissions estimates. PRELIM assumes natural gas and refinery fuel gas have similar contributions to refinery emissions via

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combustion. However, deviation in offsite gas requirements has an effect in terms of energy estimates and associated upstream impacts and should be addressed in future versions of PRELIM (offsite gas requirements match ranks at an intermediate value; wr^2=0.60). Once the deviation in total gas requirements is improved, deviation in offsite gas requirements could be enhanced by reconciliation of differences regarding onsite gas requirement/refinery fuel gas production estimates. Both improvements require detailed analysis and further validation.

PRELIM energy estimates can be beneficial for a more detailed modelling and characterization of refinery fuel gas. The outlier for offsite gas requirement in Figure 26 demonstrates the effects of PRELIM limitations to account for lighter gases separately. PRISM^{TM} and PRELIM model propane production differently. The "apples to apples comparison" required that PRISM$^{TM'}$s propane production estimates are included in the calculations of onsite gas production. This is different from the PRELIM estimates that already have propane production as part of the onsite gas or refinery fuel gas production. For some crudes the energy embedded in propane makes a difference in whether PRELIM onsite fuel gas production results in an under or overestimate. It also makes a difference in the magnitude of the deviations in such estimates. Disaggregating the refinery fuel gas characterization could help to improve estimates in energy content of the onsite fuel gas production estimates.

For the purposes of estimating refinery emissions, the proximity between both models in onsite fuel gas production, at this time, is considered acceptable (r^2=0.85 and 27% CV(RSMSD)). There is no "rule of thumb" to estimate the amount of refinery fuel gas in the industry, and it varies widely among refineries. Therefore, it is not possible to indicate which model's estimates are more accurate. In fact, both can be plausible considering the differences that arise from variations in operating conditions. The possibility that PRISM r^2 may model less or more severe hydroprocessing as has been discussed (section 8.2) also leads to deviations in onsite fuel gas production estimates. Finally, PRISM^{TM} assumes that FCC heavy products are recycled in the delayed coking process. This is not considered in PRELIM which also helps to explain the deviations in onsite fuel gas production calculated in the two models. Nonetheless, the onsite fuel gas estimates impact refinery emissions indirectly through the hydrogen requirement that is associated with the fuel gas hydrogen content. Because onsite fuel gas production/requirement estimates match ranks at between the intermediate and low values (wr^2=0.53), it warrants a more detailed investigation in future versions of PRELIM in order to improve overall refinery emissions estimates.

8.4 Hydrogen requirement

An important criterion to evaluate PRELIM performance for modelling effects of crude quality and refinery configuration on refinery GHG emissions is the capability to estimate the hydrogen requirement specific to a crude assay and configuration. Differences in hydrogen requirements will affect refinery energy use and CO_2 emissions estimates through changes in hydrogen demand from the SMR. Comparison of hydrogen requirement estimates from both models mainly compares the effects of two different modelling approaches: the PRELIM approach of global hydrogen balance using hydrogen content in feedstocks and products, and PRISM^{TM}'s use of a class of hydrogen- consuming chemical reactions to determine the hydrogen requirement to achieve olefins and aromatics saturation (e.g., using a molar ratio of 5 hydrogen atoms to one hydrocarbon molecule for saturation of aromatics or 3.3 for saturation of polyaromatics to monoaromatics) (Castañeda et al., 2011).
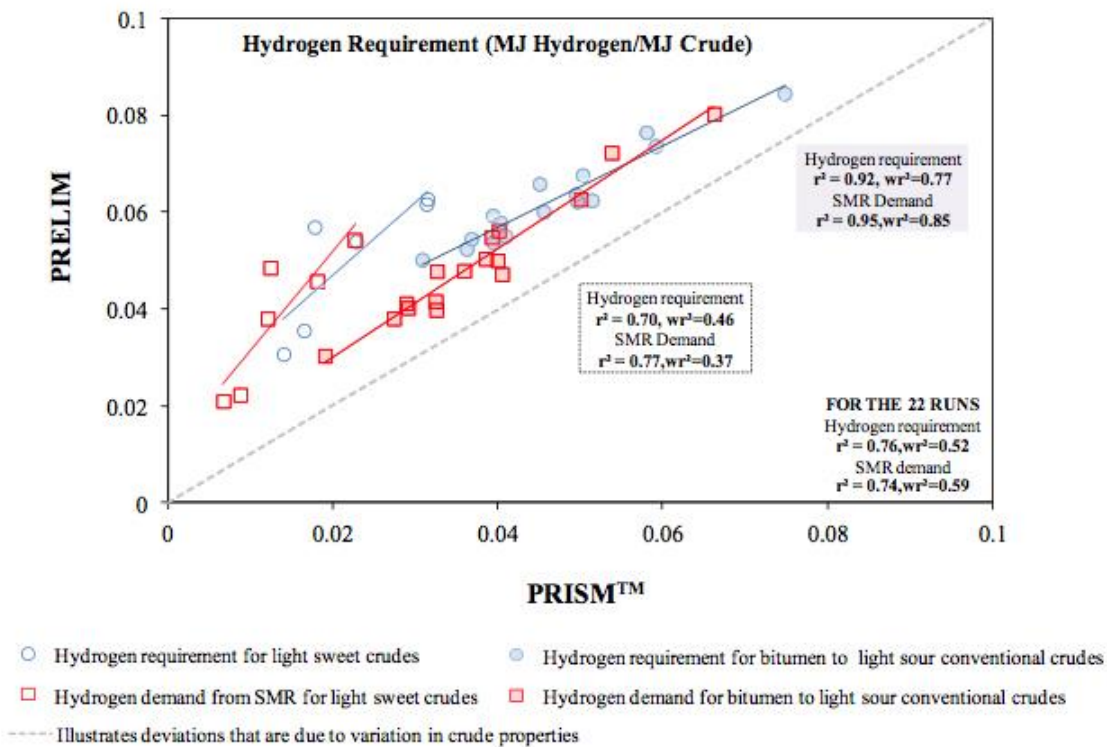
Figure 27: Comparison of fit between PRISM^{TM} and PRELIM refinery hydrogen requirement estimates

The x-axis shows PRISM^{TM}'s hydrogen requirement (MJ Hydrogen/MJ Crude), and the y-axis shows PRELIM's hydrogen requirement (MJ Hydrogen/MJ Crude). Solid lines illustrate deviations that are due to variation in crude properties.

Hydrogen demand from steam methane reforming (SMR) equals hydrogen requirement minus co-production of hydrogen via naphtha catalytic reforming. r^2: coefficient of determination, wr2: weighted coefficient of determination accounting for gradient of correlation to quantify overestimates and variability together.

The PRELIM approach is as valid as the PRISM^{TM} method to determine crude specific hydrogen requirement. Figure 27 provides three insights: 1) PRELIM consistently overestimates the hydrogen requirement and SMR demand for all runs (51% and 56% CV(RSMSD) respectively). 2) Though PRELIM's calculated hydrogen requirement is consistently high, it has the capability to reproduce PRISM^{TM}'s variability in hydrogen requirement estimates for the range of bitumen to conventional light sour crude assays (r^2=0.92 hydrogen requirement; r^2 =0.95 SMR demand). 3) There are some compromises when using different methods for analyzing the light sweet conventional and light sweet SCO assays' hydrogen requirements (r^2=0.70 hydrogen requirement; r^2 0.77 SMR demand) which limits overall model comparison. Over all runs, PRELIM replicates 76% and 74% of the "natural" variability in hydrogen requirements and SMR demand due to the quality of the crude.

The deviation in variability estimated for the hydrogen estimates and SMR demand for the light crudes can be a consequence of the different level of detail in modelling operating conditions associated with the crude properties in the two models. PRISM^{TM} may determine the level of hydrotreating and/or hydrocracking of a crude based on the structural composition of its fractions while PRELIM assumes all crudes to be treated to result in the same hydrogen specification (PRELIM does not distinguish between the structural compositions of the crude fractions).

For example, comparison of the variation in hydrogen requirement estimates for the light crudes in the deep configurations shows that PRISM^{TM} estimates more important variation than PRELIM as a result of including the hydrocracking process unit.

On the other hand, for the interpretation of the high values in the coefficient of variation of the root-mean-square deviation, it is important to recall previous discussion regarding flexibility in product yields and operating conditions that exist for refinery process units and limitations to generalize modelling correlations to all feedstock quality. In particular, for the case of hydrogen requirement, it is important to note that while the equations that PRISM^{TM} uses in its calculations (and therefore, the accuracy of the method used by PRISM^{TM} to determine hydrogen requirement) are unknown, some sets of equations used in the class of hydrogen-consuming chemical reactions method reportedly deviate from experimental data by as much as 29%. Specifically, experimental analysis found that this calculation method mostly underestimates hydrogen consumption, particularly for hydrotreating gas oil fractions (Castañeda et al., 2011). Based on the analysis of hydrogen requirements for hydrotreating processes presented in Castañeda et al. (2011), the performance of the set of equations used by PRISM^{TM} might explain the deviations when analyzing hydrogen requirement for the light crudes, relative to the PRELIM estimates. i.e., There is a set of equations available for calculating hydrogen requirement by the method of class of hydrogen-consuming chemical reactions which perform very well in predicting hydrogen requirement for hydrotreating gas oil fractions (2% deviation) while underpredicting by almost 50% the hydrogen requirement for hydrotreating naphtha fractions.

Also, it is important to consider the interrelationship between modelling parameters. The overestimates on hydrogen requirement and SMR demand are accounted in the variation in gas requirement specific to a configuration and type of crude that is assessed with an acceptable CV(RSMSD) of 24%. Similarly, hydrogen requirement is implicitly affected by the overestimated onsite fuel gas production (refinery fuel gas that has an important amount of hydrogen content) that is also assessed with an acceptable CV(RSMSD) of 27%. Nonetheless, overall model match for these estimates ranks at the limits of intermediate and low value and intermediate value (wr^2=0.52 on hydrogen requirement; wr^2=0.59 on SMR demand). Therefore, this is one of the biggest contributors to the variation at the refinery emissions estimates and should be the first area of focus for improvements in future version of PRELIM.

8.5   Other energy requirements

Overall proximity of PRELIM to PRISM^{TM} estimates for electricity and FCC coke-burned requirements is high. Consistently, PRELIM underestimates electricity and FCC coke-burned energy requirements (21% and 27% CV(RSMSD) respectively) PRELIM also replicates 87% and 99% of the "natural" variability in these estimates for all 22 runs. Overall model match on these outputs ranks at a high intermediate value (wr^2=0.85 on electricity requirement; wr^2=0.80 on FCC coke-burned requirement).

Mostly, differences in the electricity requirement are associated with differences in process unit product yields due to slight modifications in the refinery configurations when modelling PRELIM configurations in PRISM^{TM} and due to accuracy in process unit yield correlations. For example, in PRISM^{TM} recycling heavy oil derived from the FCC process unit to the delayed coking process unit is modelled, which is expected to impact the yield of intermediate products. PRELIM shows that the electricity requirement is sensitive to this modification.

In the case of the amount of FCC coke estimated to be burned, deviations are mostly due to differences in the assumed energy content of the FCC coke. It is difficult to obtain a high degree of accuracy in determining the coke

composition and therefore in its energy content because of the natural variability in composition inherent in this product. Similar to refinery fuel gas, the composition of the coke varies from refinery to refinery. It is a result not only of the process unit feed composition but also of operating conditions such as temperature. The PRELIM modelling approach does not allow for capturing differences in energy requirements due to variations in energy content associated with the FCC coke. Therefore, care should be taken when defining energy requirements for the FCC process unit that may or may not have a surplus of energy in the process unit. Nonetheless, it is the emissions derived from the FCC coke-burned which play an important role in determining overall refinery emissions rather than emissions originating from fuel savings associated with variations in the coke energy content. The co-validation results show that there is consistency between the models in the estimates of CO_2 emissions from the FCC coke-burned since deviations in FCC coke mass yield are negligible. Further development of modelling related to the FCC process unit can be useful if modelling the hydrotreating requirements for the process unit feed.

Though there are important deviations in energy estimates that should be addressed as PRELIM is improved, the variability in both models is consistent and deviations are for the most part explained. Therefore, PRELIM is considered useful/appropriate in determining reasonable estimates of energy and GHG emissions and even more powerful for comparing the relative magnitude of the energy requirements and emissions rather than absolute values.

9 Assessment of transformation methods and quality of assay data

This section evaluates the transformation methods used for converting publicly available assay data into PRELIM format (see section 5.4.1). Basically, this is a comparison between H/CAMS data and Crudemonitor data processed via PRELIM. First, the deviations between the H/CAMS and PRELIM assay parameters values for each crude in each crude assay parameter are discussed including opportunities for improvement. The quality of the data is then analyzed based on how the differences between PRELIM assays and H/CAMS assays could affect the precision and interpretation of PRELIM GHG estimates. You can learn more about the deviation between H/CAMS and PRELIM assay parameters values for each crude in Abella (2012; Table 12, Appendix C).

9.1 Assessment of transformation methods

In general, there is a good agreement between H/CAMS and PRELIM for most assay parameters (78% of parameter values have a deviation equal or below 12%), and the most significant differences can be explained by PRELIM approach of using average data. The comparison of the two different datasets demonstrates several points:

The approximations and correlations used to determine crude fraction hydrogen content and Kw factor are appropriate. Deviations are around 3% or lower for all fractions of most assays. The deviations in hydrogen content are up to 8% for the synthetic crude oil assay, and they are an exception over all the nine assays.

Temporal variation explains differences in crude distillation assay data. For example, after reviewing the synthetic crude oil assay information, it is found that the differences in the percent mass yield at a particular temperature can be up to 8% for the samples analyzed from 2004 to 2009 (used to determine the average distillation curve in current PRELIM assay inventory). Such difference in mass yield can lead to large deviations in crude fraction mass yields. The case of the synthetic crude oil assay illustrates that the approach of using average data has an important effect for fitting the distillation curve (an effect not found in other parameters), and then in the determination and interpretation of refinery GHG emissions specific to a crude.

The approximation to estimate MCR is suitable. For most assays, the deviations in the values for this parameter are consistent with what is found when analyzing the approximation using the 50 confidential assays tested. The largest deviations in the values of this parameter result from disagreement between the sources of data. For the light sweet synthetic crude assay, CCQMP reports neither a vacuum residue fraction nor an MCR in this fraction while H/CAMS does report them. Temporal variation does not explain the large deviations in sulphur, nitrogen, and API estimates (nitrogen is present in the PRELIM assay inventory only for information purposes; PRELIM calculations neglect its effect on hydrogen requirements based on evaluation of its impact on GHG emissions estimates). Table 12 in Appendix C of Abella (2012) shows that for some cases the deviations in these crude assay parameters are beyond 20%. CCQMP data show that the deviation (calculated in percentage as 100 times the standard deviation of parameter values divided by average of those parameters) for those parameters are mostly below 10% for different crudes in different fractions (fractions wider than the fractions used in PRELIM). Deviations higher than 10% (as is the case for PRELIM assay compared to H/CAMS assays) happen occasionally in CCQMP data for sulphur content and are up to 15%.

The polynomial regression method used to determine sulphur and API (also nitrogen) of the crude fractions could have been affected by the number of observations but also due to the use of less detailed

data to develop a more detailed assay. The large deviation in the fractions' sulphur content values happens for the assays derived from CCQMP data rather than for the assays obtained from confidential sources. It suggests that a more detailed assay (i.e., assay information for less wide fractions) can improve the accuracy of the regression method employed.

Alternative methods to the polynomial regression can be explored in order to obtain better API estimates for the distillation residue fractions. The use of conversion of distillation curves on mass basis (simulated distillation methods) to distillation curves on volume basis could be an option to be investigated and to obtain the required accuracy in the volume yields of each crude fraction. Sulphur content has a minor or negligible effect in PRELIM response; therefore, higher accuracy in this parameter at this stage of model development is not needed.

9.2   Overall Quality of PRELIM Assay Data and Interpretation

The quality of the assay data is considered meaningful for the purposes of estimating the refinery GHG emissions estimates. The deviation in overall refinery GHG emissions (for all 99 runs) is 5% CV(RSMSD). Figure 28 shows that in general, using two groups of assay data (H/CAMS and PRELIM), proximity in PRELIM GHG estimates for the overall refinery emissions is high. In most cases, using PRELIM assay data leads to a slight underestimation of the overall refinery GHG emissions (only 1 out of the 9 assays showed overestimation for 3 out of 11 refinery cases tested); however, the deviation is not higher than 12% (light synthetic crude oil assay: 11% CV(RSMSD) when measured against estimates using H/CAMS assay data). Because the comparison of assay data involves crudes of different quality, it is expected that a similar performance will result when the larger assay inventory is explored. While there are deviations resulting from a comparison of the two datasets, such deviations do not play a large role in the overall refinery emissions estimates. This suggests that the transformation methods proposed and implemented in PRELIM are robust and can be used for PRELIM assay inventory.
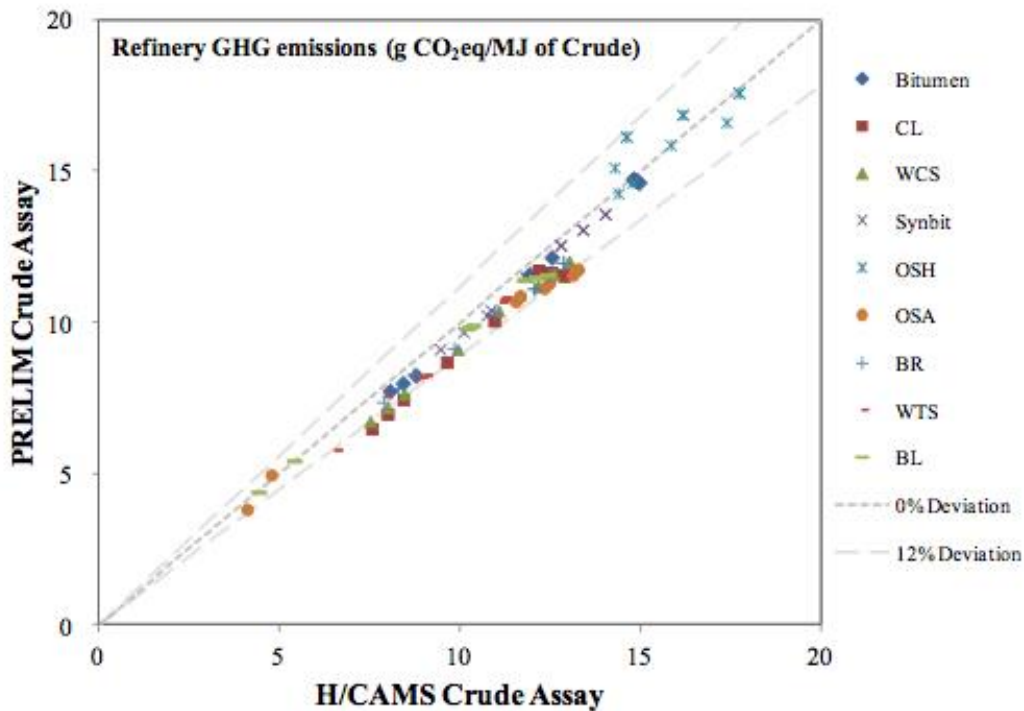
The x-axis shows the PRELIM's GHG estimates (g CO_{2eq}/MJ) using H/CAMS assay values, and the y-axis shows PRELIM's GHG estimates (g CO_{2eq}/MJ) using PRELIM crude assay inventory. Diagonal dotted lines illustrate deviations that are due to variation in crude properties.

It is advisable to consider that current PRELIM crude assay inventory uses average data which can affect the assessment of crude assay quality. In Figure 28, the deviation in PRELIM GHG estimates for the synthetic crude oil assay result from individually small deviations in hydrogen content of each fraction with relatively large deviations in fraction volume yield (i.e., deviations in crude fraction hydrogen content are up to 8% and deviations in crude fraction volume yield are up to 41%). The deviations in hydrogen content of the crude fractions are in the expected margin of error for hydrogen content estimates using analytical methods (Choudhary et al., 2008). However, deviations in crude oil distillation curve information warrant attention and must be explained by temporal variation. The significance of using average data is mostly related to analyzing crude-specific GHG emissions for a refinery product. Figure 29 shows that using the different assay data (H/CAMS and PRELIM), the deviations in gasoline and diesel GHG emissions estimates for all crudes is mostly below 10% (for 67% of the estimates; all 11 cases and 6 out of 9 assays). However, when analyzing GHG emissions specific to the case of the light synthetic crude oil assay a large deviation exists (29% CV(RSMSD) for gasoline and 75% CV(RSMSD) for diesel GHG estimates). The deviation results from the combined effect of the deviations in hydrogen content of the fractions and in the distillation curve, and it can be interpreted as the effect of temporal variation on the crude assay information. Outliers in Figure 29 specific to two diluted bitumen assays are not considered relevant because they correspond to a "hypothetical" case when the crudes are run in a medium refinery configuration (hypothetically as they are not currently being processed in this type of refinery); however, the deviation demonstrates the effects of average crude distillation curve data as well. The deviations for those diluted bitumen assays are mainly related to deviations in their distillation curves. GHG emissions estimates for a crude using PRELIM assay data will differ somehow from estimates using assay data from a single sample; therefore, it is important to consider that PRELIM assay data will represent an average quality of these crudes.
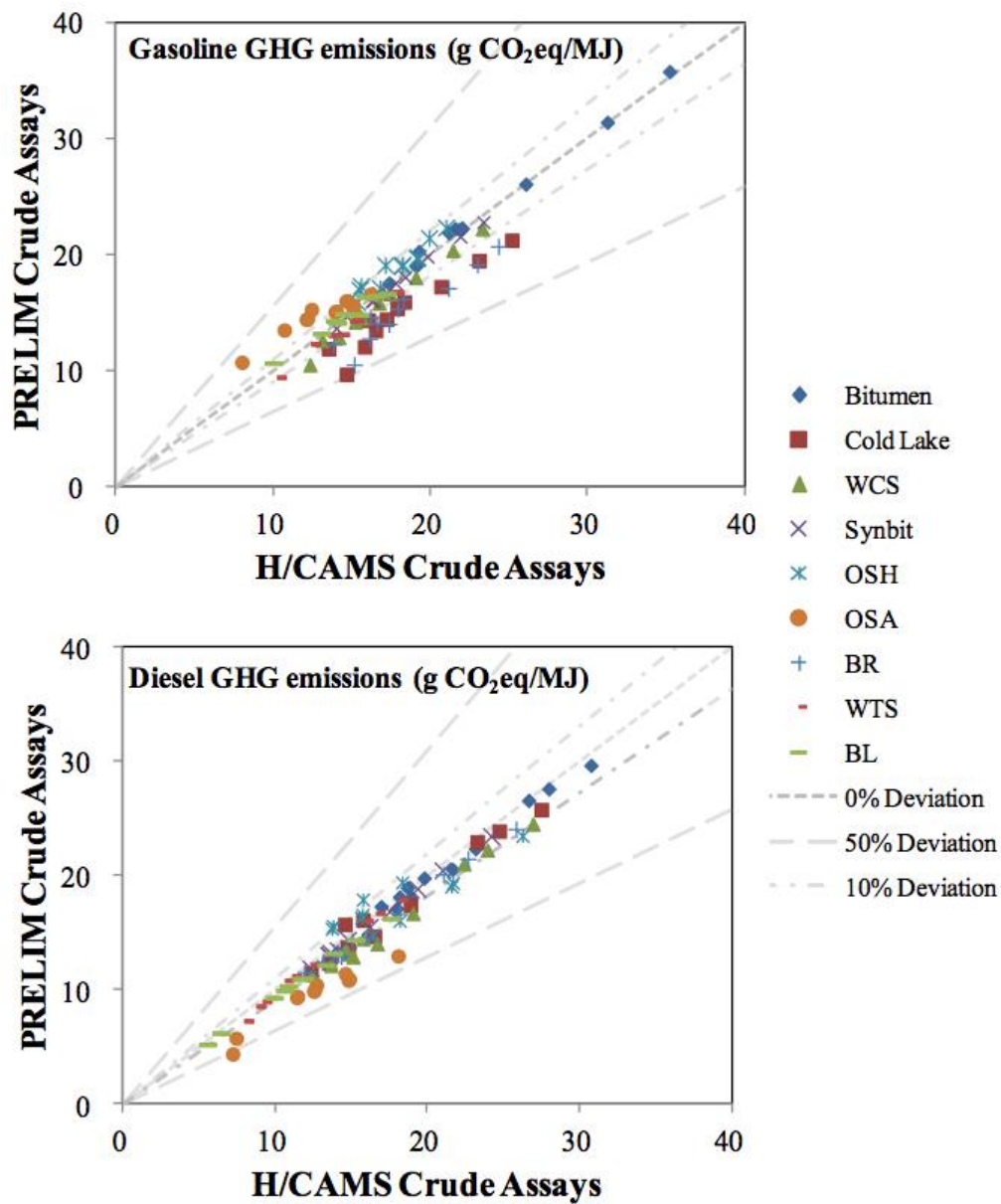
Figure 29: Comparison of fit between PRELIM (a) gasoline and (b) diesel GHG emissions estimates using H/CAMS and PRELIM crude assay data

The x-axis shows the PRELIM's GHG estimates (g CO_{2eq}/MJ) using H/CAMS assay values, and the y-axis shows PRELIM's GHG estimates (g CO_{2eq}/MJ) using PRELIM crude assay inventory. Diagonal dotted lines illustrate deviations that are due to variation in crude properties.

9.3 Quality of PRELIM Crude Specific Assay Data

GHG emission estimates for the life cycle of petroleum products are impacted by natural and technical variability on data and methods. The quality of data can cause uncertainty in the emissions estimates. Overall, data quality within PRELIM is impacted by 2 major sources of variability:

1. Crude Assay Characterization Methods:

- Natural variability due to oil chemistry complexity, reservoir specific properties, seasonality, and time of production over the lifetime of a well.
- Technical wide-ranging variability in crude oil sample types, sampling methods, and analytical methods.
- Cumulative effects of the natural and technical variability factors in the implementation of a standard protocol to transform the assay data and obtain the PRELIM assay inventory.

2. Characterization of real-world operations:

- Refinery operations include crude blending and variations in process severity that impact intermediate and final product slate (thus, energy use and emissions associated) in response to market demand.
- Refining operations include variations in process energy efficiencies.

For evaluating new assay data incorporated within PRELIM assay inventory (that add to the evaluation of the transformation method conducted on Western Canadian data), a set of critical data quality elements were identified that consider the expected variability. For the purposes of PRELIM, the relevance of the assay data depends on how it ranks for the following elements:

- Reliability and reproducibility/precision: Data quality improves as an additional set of information for particular crude (i.e. assay characterization data) becomes available. The impact of data variability could be further evaluated, and the data set can be selected based on project data quality criteria.
- Consistency and completeness: Data quality improves as the type of data about crude assays available to represent a specific crude compared to other crudes meets PRELIM modeling needs. It implies that less transformation and/or assumptions must be conducted that could bias results.
- Accuracy: Data quality improves as the proximity of results to real performance is expected. Current PRELIM modeling methods are anticipated to have less impact and/or bias in the results.
- Vintage: Data quality improves as it is more recent and becomes more relevant to provide current picture of oil world performance. Old data can still be relevant when the use of the information is to inform potential changes overtime. Data vintage can provide context for interpretation of results.

An assessment of the data quality on PRELIM assay inventory is conducted based on the critical data quality elements and a set of criteria and indicators to score data used by PRELIM as indicated in Table 11.

Table 11: Indicators and Ranking used to assess PRELIM crude specific assay data quality

Data Quality Element	Criteria Indicator	Rank
Reliability and reproducibility	**1. Representativeness**	
	Assay data selected from several published samples	3
	Assay data have been reviewed and prepared by experts (accepted quality within commercial/market intelligence groups)	2
	Assay data represented by one sample, proxy assay, and/or assay without information about sampling/data collection methods	1
	2. Vintage	
	Assay data are recent (e.g., last 10 years)	3
	Assay data are aging (e.g., last 10 to 30 years)	2
	Assay data required to be updated (e.g.,>30 years)- Proxy assay	1
	3. Transparency and validity	
	The source is a public data set or peer-reviewed technical literature	3
	The source is a private data source (uncommon) or a web reference (due to uncertain provenance of general web data)	2
	Several data sources validated with private information - Proxy assay	1
Consistency and Completeness	**4. PRELIM minimum assay data transformations**	
	4.1 True Boiling Point	
	TBP number of cuts equal or > PRELIM	3
	TBP number of cuts < PRELIM	2
	4.2 Hydrogen	
	Hydrogen content in fractions is included	3
	Hydrogen content in fractions is not included but hydrogen content of the whole crude is	2
	No Hydrogen data	1
	4.3 Carbon Residue	
	CR data is included	3
	CR data is not included	2
Accuracy	**5. Certainty in applicable refinery configuration**	
	Heavy and medium crudes (medium and deep conversion)	3
	Light crudes (hydroskiming)	1
	6. PRELIM hydrogen modelling approach impact	
	Heavy and medium crudes	1
	Light crudes	2

After the assessment of data quality, three different data quality levels were found to synthesize the variability in information used within PRELIM Assay inventory.

- Below Minimum Quality: Data provides enough information to use standardized methods of analysis to make only a basic representation of crude performance.
- Meeting minimum requirements: Data are relevant for the purposes of the analysis, and complies with most modeling needs. Some standardized methods are applied.
- Exceeding minimum requirements: Data provide additional information for modeling that improve reliability and/or allow for further evaluation of a crude.

Figure 30 presents a data quality assessment for 75 crudes that include all data sources used for PRELIM v1.1 data assay inventory. Assays out of the assessment are expected to rank within the minimum requirements as they derived from same data sources used for characterization of the crudes included in this assessment. Only 2 assays are considered currently below minimum quality requirements and those are Margham Light_COA proxy Eagleford Volatile and Statoil Snohvit Condensate proxy for Eagle Ford. Their rank is explained by the fact that they are proxy assays used to represent expected quality of crudes from the Eagle ford tight oil operations rather than specific assays of the crudes.
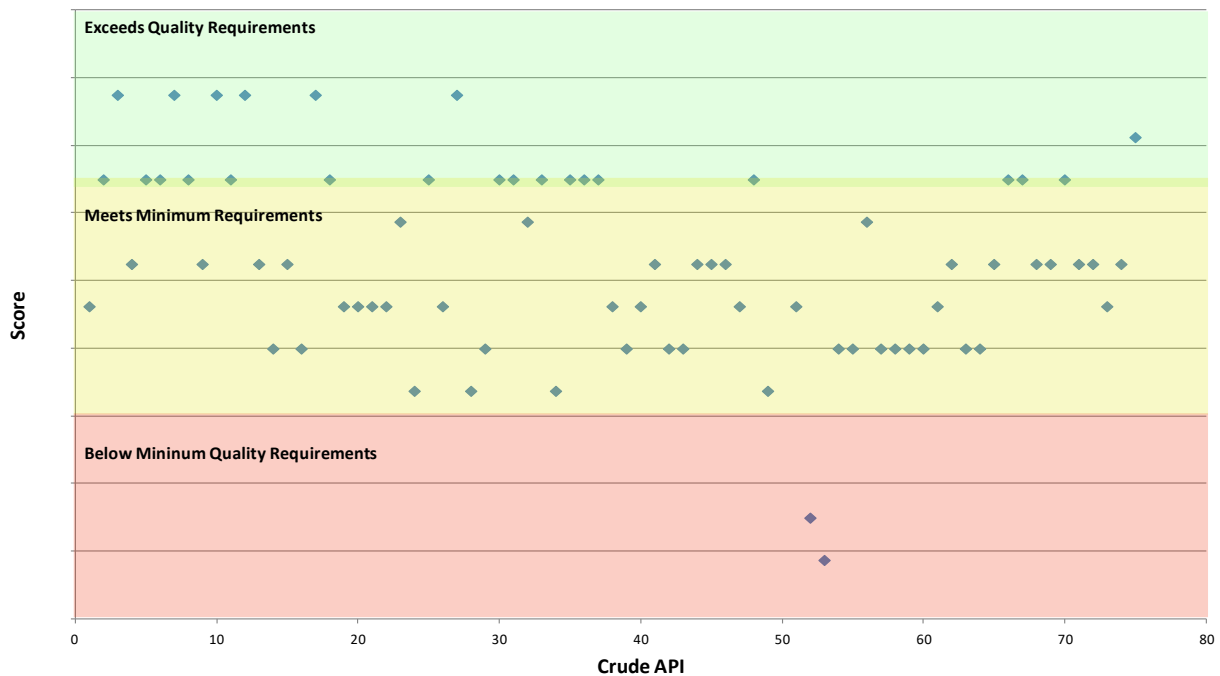
Figure 30: PRELIM crude specific assay data quality assessment including all PRELIM v.1.1 data sources

10 Comparison of PRELIM greenhouse gas predictions with estimates in the literature

Straightforward comparison of PRELIM results with the literature is not possible, due to the use of different allocation methods, system boundaries, assumptions about process energy requirements, etc.

A National Energy Technology Laboratory (NETL) study (NETL, 2009) reports refinery emissions of approximately 13 gCO_2e/MJ gasoline for Venezuelan upgraded bitumen and Canadian oil sands. These estimates are lower than what PRELIM reports (approx. 21 gCO_2e/MJ of gasoline). However, NETL study reports similar emissions for other conventional and nonconventional crudes which implies that the model used did not differentiate between crudes based on detailed assay information. For example, NETL report does not include emissions from some of the most carbon intensive imported crude oils such as Venezuelan Heavy were not included due to modelling uncertainties. In addition, linear relationships to relate GHG emissions from refining operations based on API gravity and sulphur content of the whole crudes was assumed.

A Jacobs study (Jacobs Consultancy, 2009) reports total refinery GHG emissions of approximately 83 and 72 kg CO_2e/bbl of crude for a bitumen with an API of 9, and a dilbit with an API of 20, respectively, which is consistent with the results of PRELIM (total GHG emissions of approx. 86 and 65 for a bitumen and a dilbit with similar APIs). Also, an IHS Energy study (IHS Energy, 2014), reports refinery emissions of 81 and 71 $kgCO_2e/bbl$ of crude for bitumen and dilbits.

Compared to the results of a report prepared by Life Cycle Associates, LLC study (Life Cycle Associates, LLC, 2009), that reports refinery GHG emissions of approximately 10 gCO_2e/MJ of gasoline for bitumen, PRELIM reports higher GHG emissions (approx. 21 gCO_2e/MJ of gasoline). Inclusion of the indirect upstream emissions as well as the specific assumptions that exist for different processes (i.e., unit processes, power plants, allocation methods among others) in PRELIM may explain the difference in these estimates between these studies (see Abella and Bergerson, 2012).

The comparison made between the results of PRELIM and other sources for bitumen and dilbit is summarized in Table 12.

Table 12: Comparison of GHG emissions predicted by PRELIM and GHG emissions reported in the literature for Bitumen and Dilbit

Crude	Bitumen		Dilbit	
GHG emissions	kg/bbl of crude	gCO_2e/MJ of gasoline	kg/bbl of crude	gCO_2e/MJ of gasoline
PRELIM*	86	21	65	15
IHS Energy	81	-	71	-
Jacobs	83	-	72	-
NETL	-	13	-	-
Life Cycle Associates	-	10	-	-

*PRELIM estimates GHG emissions in the range of 66 - 72 $kgCO_2e/bbl$ and 86-91 $kgCO_2e/bbl$ for the dilbit and bitumen assays that are currently available in the model.

Appendix A: Changes and updates from previous versions of PRELIM

- An initial version of PRELIM was published in 2012 in the Environmental Science & Technology Journal (Abella P. and Bergerson J., 2012).
- PRELIM version 1.0 was released on March 6, 2015.
- PRELIM version 1.1 was released on Sept 15, 2016.
- PRELIM version 1.2 was released on October 24, 2017.
- PRELIM version 1.2.1 was released on December 8, 2017.
- PRELIM version 1.3 was released in April 2019.
- PRELIM version 1.4 was released in May 2020.
- PRELIM version 1.5 was released in October 2021.

Changes and Updates from PRELIM v.1.4 to PRELIM v.1.5

Major Expansions and Updates

Direct separation of Naphtha, Atmospheric Residual (AR), Light Vacuum Gas Oil (LVGO), and Heavy Vacuum Gas Oil (HVGO) as products for sale is now available. Their production can be accessed via the `CokingRefineryCalcs` worksheet Cells K132, P45, K549, and L549 and the `HydroRefineryCalcs` worksheet Cells M119, Q45, K523, and L523, respectively. Users can choose if emissions are allocated to them on the `Main Input & Output` sheet.

A region selection function is now available, including global average (default), North America, Latin America, the Middle East, Asia & Oceania, Russia & Europe, and Africa. Users can choose where refining takes place. The energy requirement and yield pattern of main process units are updated accordingly for each region using proprietary industry datasets. See the `Constants` sheet for more details.

A complete refreshment of kerosene/jet fuel production. In previous versions of PRELIM, kerosene/jet fuel only comes from kerosene hydrotreater. Now with PRELIM 1.5, kerosene/jet fuel can be produced from the following pathways: a) direct separation from the Atmospheric Distillation Unit, b) hydrotreated kerosene/jet fuel from kerosene hydrotreater (same with earlier versions), c) production from diesel hydrotreater, and d) production from gas oil hydrocracker (premium quality). These pathways can be accessed via the `CokingRefineryCalcs` worksheet Cells R43-W56, I262-K271, O321, and I479 and the `HydroRefineryCalcs` worksheet Cells S43-X56, K252-M261, P317, and I453, respectively. You will notice that we have updated Atmospheric Distillation kero to blending, KHT, and DHT. We have also updated DHT and Hydrocracker yield directly to jet blending.

Minor Changes

- Added an on/off switch for naphtha hydrotreater (NHT), kerosene hydrotreater (KHT), and diesel hydrotreater (DHT). Updated hydrotreated jet/kerosene and diesel density.
- Enabled a second LHV and HHV prediction method based on American Petroleum Institute-Technical Data Book- Petroleum Refining. (See Energy & Unit Conversions Tab, Cell F46).
- Fixed the calculations of asphalt property specifications.

Changes and Updates from PRELIM v.1.3 to PRELIM v.1.4

Major Expansions and Updates

Most hydrogen consumed by refineries is either produced onsite or purchased from offsite via steam methane reformer, which is emissions and cost intensive. Hydrogen consumption therefore represents one of the most important contributors to not only refining GHG emissions, but also refinery operating costs. On a global scale, other than hydrocracking, almost half of a refinery's hydrogen demand is used for hydrotreating operations, where hydrogen is used for removing unwanted impurities from products and improving product quality. Therefore, being able to predict hydrogen consumption rates of hydrotreaters plays a key role in determining the overall refinery GHG emissions. PRELIM estimates hydrotreater hydrogen use mainly based on the difference between input and output hydrogen content.

$$H_{consumed} = 1.05 * (H^1_{liquid} - H^0_{liquid} + H^1_{H_2S} + H^1_{NH_3} + H^1_{HCgas})$$

However, previous versions of PRELIM set hydrotreater output hydrogen content as constants based on industry expert opinions, which may not reflect the actual variations of hydrogen caused by different types of refineries and different crude slates. In PRELIM v1.4, thanks to proprietary industry datasets, these output hydrogen content values have been calibrated to be linearly associated with input hydrogen content rather than constants. In other words, for each hydrotreater, multiple linear regression equations are obtained and adopted for all types of refineries (e.g., hydroskimming, medium FCC, deep FCC) improve accuracy. Detailed steps are summarized as follows:

Step 1: For each type of hydrotreater in each refinery configuration, collect hydrogen consumption data ($H_{consumed}$) from corresponding refineries available from industry datasets. For example, for naphtha hydrotreater in the medium conversion FCC refineries, there are 81 consumption datapoints available from industry datasets.

Step 2: Run all selected refineries from Step 1 in PRELIM by using their transformed crude slates. Record hydrotreater inflow properties of the selected hydrotreater including $H\%^0_{liquid}$, sulfur content, and nitrogen content in wt.% for all selected refineries.

Step 3: Record H^0_{liquid}, $H^1_{H_2S}$, $H^1_{NH_3}$, and H^1_{HCgas} for all selected refineries.

Step 4: According to the above equation, calculate H^1_{liquid} and then $H\%^1_{liquid}$ for all selected refineries.

Step 5: Generate a linear regression equation based on the $H\%^0_{liquid}$ and $H\%^1_{liquid}$ of all selected refineries.

Step 6: Repeat Steps 1-5 for all other hydrotreaters and refinery configurations.

In this way, we believe PRELIM v1.4 can better predict the hydrogen consumption rates by hydrotreaters and calculate the associated GHG emissions. However, this is ongoing research and we hope to further improve these estimates in future versions of PRELIM.

Minor Changes

- Gas oil hydrocracker API-naphtha regression is updated to accommodate extra light inputs by using neural network predictions. Existing dataset from Gary et al. (2007) is used for training this feedforward

neural network by using feed API (<36º) as input and naphtha yield as output. Then the developed neural network is used to extrapolate naphtha yield from feed that has a higher API (39º).

- Added a function to either produce RFG as a product or consume it onsite; also fixed the calculations of energy use and emissions when RFG is produced and sold rather than consumed onsite (see details on Page 14).
- Added a function that can directly separate AGO from Atmospheric tower as fuel oil. This reduces the emissions factor of fuel oil as it does not have to be processed by FCC or GOHC as before.
- Set FCC post hydrotreater (FCCPHT) as the default option. FCC Feed Hydrotreater (83 out of 363 refineries worldwide) is not as widely deployed as FCCPHT (216 out of 363 refineries worldwide) because it may not be economically worthwhile to treat all incoming FCC feed, unless more high quality gasoline is desired from FCC than diesel.

Changes and Updates from PRELIM v.1.2.1 to PRELIM v.1.3

Major Expansions and Updates

Prior to this update, PRELIM was able to provide results for energy use and greenhouse gas emissions from petroleum refineries with a level of detail suitable for most LCA studies in support of policy decisions. The model was updated to add more criteria in regards to air pollutants, hazardous air pollutants, releases to water, releases to land, and managed wastes reflecting 2014 reported releases and waste management practices using data from the U.S. Environmental Protection Agency Greenhouse Gas Reporting Program, National Emissions Inventory, Discharge Monitoring Reports, and Toxic Release Inventory together with process unit capacities and fuel consumption data from the U.S. Energy Information Administration (US EIA). As in earlier versions of the model, these expanded release inventories are calculated for each subprocess and are allocated to refinery products according to user specifications. These relationships are summarized in an output matrix added to PRELIM v1.3 to facilitate flow tracking and quality assurance (see the `Input – Output Allocation Calculations` section in the `CokingRefineryCalcs` spreadsheet. The variability of refinery subprocess release factors is characterized using lognormal distributions with parameters set by the distribution of release factors across facilities. The US EPA Tool for the Reduction and Assessment of Chemical and Environmental Impacts (TRACI) life cycle impact assessment (LCIA) method is used together with the updated inventory data to provide impact potentials in the PRELIM dashboard interface. Full inventories for refinery products are assigned via PRELIM based on releases from individual refinery subprocesses. Emissions from refinery subprocess are assigned in one of the following three methods:

1)   Heat-related emissions. Combustion emissions resulting from the generation of heat or steam from fuel combustion are assigned to refinery products based on the aggregate heat demand. Heat and steam demand are calculated by PRELIM for each refinery product by summing demands at each process unit.

a.   Process emissions from hydrogen production via SMR and combustion emissions for the heat and steam demand for the SMR are allocated in a similar manner. PRELIM calculates aggregate hydrogen demand for each refinery product by summing demand at each process unit.

b.   Emissions from electricity generation off-site, if included, are calculated in a similar manner. PRELIM calculates aggregate electricity demand for each refinery product by summing demands at each process unit.

2)   Process unit emissions. Process emissions from refinery process units are assigned to downstream products using an input-output approach which reflects the assay and model parameters selected.

3)   Support services emissions. Process emissions from support services and releases from managed wastes are assigned directly to refinery products based on the appropriate allocation of the crude flow through the facility.

Full inventories and TRACI impacts are provided for each refinery product on a per MJ product basis. An inventory is also reported per barrel of crude processed. Release inventories at the subprocess level enable greater responsiveness to variable selection within PRELIM, such as refinery configuration and allocation to specific refinery products. The updated version also provides a template to allow users to import PRELIM inventory results into OpenLCA (Ciroth, 2007), an open-source LCA software, as unit process datasets. **Complete details of the changes from PRELIM v1.2.1 to PRELIM v1.3 can be found in (Young et al., 2019).**

The following impact categories are now included in PRELIM:

- Global Warming Potential (GWP), kg CO_2 eq.
- Photochemical Ozone Formation Potential (POFP), kg O_3 eq.
- Acidification Potential (AP), kg SO_2 eq.;
- Particulate Matter Formation Potential (PMFP), kg $PM_{2.5}$ eq.
- Eutrophication Potential (EP), kg N eq.
- Ozone Depletion Potential (ODP), kg CFC-11 eq.

In addition to the inclusion of new emissions calculations for the new impact categories included in PRELIM v1.3, the new calculation methods also resulted in changes in some emissions factors previously used in PRELIM v1.2. *Table 13* compares the emissions factors used in PRELIM v1.2 with the new values used in PRELIM v1.3.

Table 13 Comparison of emissions factors for sources found in PRELIM v1.2

	PRELIM v1.2	PRELIM v1.3	Pct Change from v1.2	Net Change GWP
NG Combustion (g / MJ)*				
CO_2	56.3	58.2	3.3%	3.3%
CH_4	1.04E-3	3.22E-3	210%	0.1%
N_2O	1.04E-3	6.24E-4	-40%	-0.2%
FCC Catalyst Coke Combustion (kg / m³)				
CO_2	120.4	153.1	27%	27%
CH_4	4.89E-3	4.76E-3	-2.7%	0%
N_2O	1.22E-3	9.38E-4	-23%	-0.1%
SMR (kg / m³)				
CO_2	0.670	0.663	-1.1%	-1.1%

Minor Changes

- Updated tabulated and graphical presentation of results in the results spreadsheets.
- Expansion of PRELIM's assay inventory to include 144 crude oil assays in total.
- Addition of a template to allow for exporting the results to OpenLCA.

- Changes in the default settings. The following options are the new default choices in PRELIM v1.3:
  - SMR hydrogen purification options: PSA
  - Cogeneration Unit: NGCC-CHP (Gas turbine & Steam Turbine)
- Summary of the subprocess allocation relationships in an Input/Output allocation matrix (see the `Input – Output Allocation Calculations` section in the `CokingRefineryCalcs` spreadsheet).
- Export to OpenLCA: PRELIM v1.3 provides a template to allow users to directly import PRELIM inventory results into OpenLCA as unit process data sets. This enables rapid generation of refinery inventories as a component of larger LCA models or for use with alternate LCIA methods or characterization factors.
- Option to allow exporting of the "Results Single Assay" spreadsheet into a new Excel workbook. This can be achieved by clicking the "Export the results into a new workbook" button on the "Results Single Assay" spreadsheet.

Changes and Updates from PRELIM v.1.2 to PRELIM v.1.2.1

No major expansions or changes occurred between PRELIM v.1.2 and PRELIM v.1.2.1. The changes only include fixing the following issues in PRELIM v.1.2:

- Fixing broken links; some minor changes were made. Results from the previous version remain valid.
- Allocation to liquid heavy ends; this issue would only affect the results if allocation to liquid heavy ends was selected by the user.

Changes and Updates from PRELIM v.1.1 to PRELIM v.1.2

Major Expansions and Updates
- Advanced features
  1) FCC feed hydrotreater options:
     - Based on feedback from industry experts, this modelling option was added to allow for evaluating alternative refinery configurations that do not hydrotreat the FCC feed (referred to as pre-hydrotreating in the model), and instead utilize a hydrotreater to hydrotreat the FCC gasoline (referred to as post-hydrotreating in the model). Calculations associated with FCC feed hydrotreating are disabled, and the FCC post hydrotreater calculations become activated in the model when using this feature in the `Main Input & Output` worksheet.
  2) Product slate optimization procedures:
     - Product slate optimization to allow for altering of the ratio of gasoline to diesel in the product slate of the refinery.
     - Product slate optimization to allow for maximizing or minimizing of the share of gasoline in the product slate.
     - Product slate optimization to allow for altering of all products in the product slate of the refinery.
     - Swing jet fuel/kerosene fraction to diesel fraction at the distillation column to allow for modelling current U.S. jet fuel/diesel production ratio.

     These procedures can be found on the `Expert Input` worksheet of the model.
  3) SMR hydrogen purification options:

- Newer hydrogen production plants are more likely to employ PSA hydrogen purification rather than Amine CO_2 removal. The capability to choose whether to use PSA or Amine CO2 removal has been added to this version of the model.

4) Improved hydrotreater output assumption calculations:
   - The logic that adjusts the hydrotreater output hydrogen content assumptions are modified to ensure that enough hydrogen is always added to remove sulphur and nitrogen in from the input stream to the hydrotreaters.

5) Cogeneration options:
   - This option allows for the evaluation of using gas turbine, microturbine, reciprocating engine, steam turbine, fuel cell or NGCC cogeneration technologies to meet refinery electricity requirements. This feature can be activated in the `Main Input & Output` worksheet.

6) Asphalt Production Configuration:
   - A configuration option that increases the output of asphalt, which only includes a desalter, atmospheric furnace and tower, and vacuum furnace and tower

7) Option to allow specifying a cetane number for hydrotreated diesel or an octane number for catalytic naphtha reformer gasoline
   - New features are added in the "Expert Input" spreadsheet within the model that allows the user to set a specific cetane number for hydrotreated diesel, of a specific octane number for catalytic naphtha reformer gasoline in the model

Minor Changes

- Assumption of Kw for delayed coking gas oil changed from 12 to 11.5 in the `CokingRefineryCalcs` and `HydroRefineryCalcs` worksheets. The change does not impact previous version of PRELIM as the assay inventory was narrow and the input to hydrocracking and FCC units remain within the process unit yield curves.
- Dynamic calculations for RFG emission factor added for small boilers.
- Hydrocracking refinery RFG calculations are now dynamic.

Corrections

- The petroleum fraction enthalpy of the Vacuum Tower furnace in the `CokingRefineryCalcs` and `HydroRefineryCalcs` were corrected to include the vacuum residue to heavy fuel oil and asphalt streams. This change causes a slight increase (a maximum difference of 5.86 kg/bbl and an average difference of 1.15 kg/bbl) to the total refinery emissions for medium conversion configurations.
- The calculation of the vacuum residue product to heavy fuel oil Kw in the `CokingRefineryCalcs` and `HydroRefineryCalcs` was corrected by taking into account the mass flow of the asphalt stream.
- For all hydrotreaters, nitrogen is now being taken into account for the liquid mass balance. Note that it is negligible in previous calculations, however, it is necessary in order to set hydrogen requirements to zero for the Asphalt Configuration.
- The products energy output of sulphur was removed from the Total Refinery Summation in the `CokingRefineryCalcs`
- In the HydroRefineryCalcs worksheet, the reference links for cells N1252 and O1252 are corrected from O1588 to G1588 and O1589 to G1589, respectively.
- The formula for the enthalpy calculation for the vacuum residue stream feed into the coker (AL250) is corrected to use the density, rather than the API.

- RFG energy content is now correctly calculated when HHV is selected.
- Dynamic calculations per MMBtu and per MJ are now correct

Changes and Updates from PRELIM v.1.0 to PRELIM v.1.1

Major Expansions and Updates

- Assay inventory of the model has been expanded and now includes 112 crude oil assays.
- Advanced features:
    1) Disabling the FCC feed hydrotreater:
        - Based on the feedback from industry, this modelling option was added to the model to allow for evaluation of alternative refinery configurations that do not use FCC feed hydrotreatment. Calculations associated with FCC feed hydrotreating are disable in the model when using the feature in the `Main Input & Output` worksheet.
    2) Expanded product slate that includes LPG, petrochemical feedstocks, and Asphalts:
        a. General modifications
            - Market value of LPG, petrochemical feedstocks and asphalt into the `Constants` worksheet
            - New products are presented on PFDs worksheets
            - Allocation switches on/off added on `Main Input/Output` worksheets
            - System-level calculations added to calculate individual product energy demand and GHG contribution, results displayed in the `Results Single Assay`, `Results All Assays` and `Main Input/Output` worksheets.
        b. LPG and Petrochemical Feedstocks modifications
            - Molecular breakdown of off-gas streams (carbon-rich portion only, not including sour gas) are included into the `Constants` worksheet.
            - LPG is assumed equal to total propane and butane (both isomers).
            - Petrochemical feedstock is equal to total ethylene, propylene and butylene.
            - Calculations added to end of `CokingRefineryCalcs` and `HydroRefineryCalcs` spreadsheets to calculate amount produced, properties, and allocation.
            - Calculations added to the `Emission Factors` worksheet to account for changes in refinery fuel gas composition after recovery of LPG and petrochemical molecules; 100% combustion efficiency (i.e., 100% carbon conversion to CO_2) was assumed.
        c. Asphalt modifications
            - Slider bars for asphalt production added to the `Main Input/Output` worksheet
            - Default amount calculated by correlation (based on vacuum tower capacity), maximum amount equal to 15% of vacuum tower capacity.

Additional details regarding the expansion of product slate in PRELIM v.1.1

Impacts of LPG, Petrochemicals, and asphalt modelling options

PRELIM v1.1 incorporates modelling options that allow for estimating potential production of LPG, petrochemical feedstocks, and Asphalt. The implications of these modelling options in the GHG emissions of a crude are illustrated by applying LPG and petrochemical feedstock modelling options to a crude (e.g. Iraq_Basra crude) and running a deep conversion (FCC) coking refinery. The following breakdown of off-gas components for both, PRELIM v1.1 default off-gas allocated to RFG and the alternative modelling option is illustrated in Figure 31.
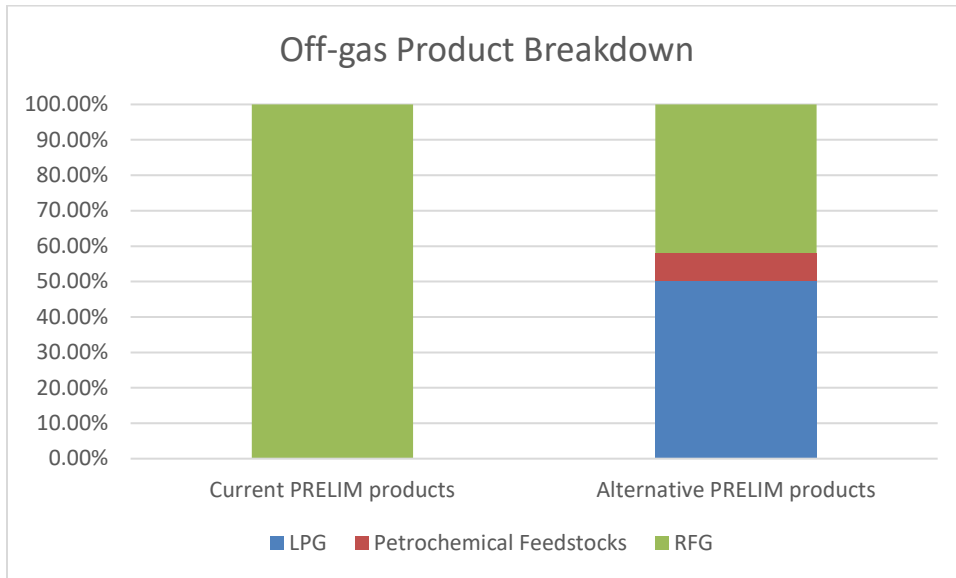
Figure 31 Iraq_Basra Off-gas product breakdown

In this example, the amount of petrochemical feedstock produced (from naphtha components) is approximately 1/5 of the amount of LPG produced, which is in the same order of magnitude with refinery net production in the US (EIA, 2015). In this way refinery increases product value; however, onsite fuel availability decreases an additional fuel will have to be imported to the refinery to meet process energy requirements.

In PRELIM the actual production of LPG and petrochemicals is specific for each crude based on its crude distillation curve that defines process units' feed volume flow at each refinery configuration. As a result, changes to a refinery's total GHG emissions when activating the LPG and petrochemical feedstock production options are also defined based on crude and configuration. Figure 32 below shows these differences in emissions when running light, medium and heavy crudes through their default configurations.
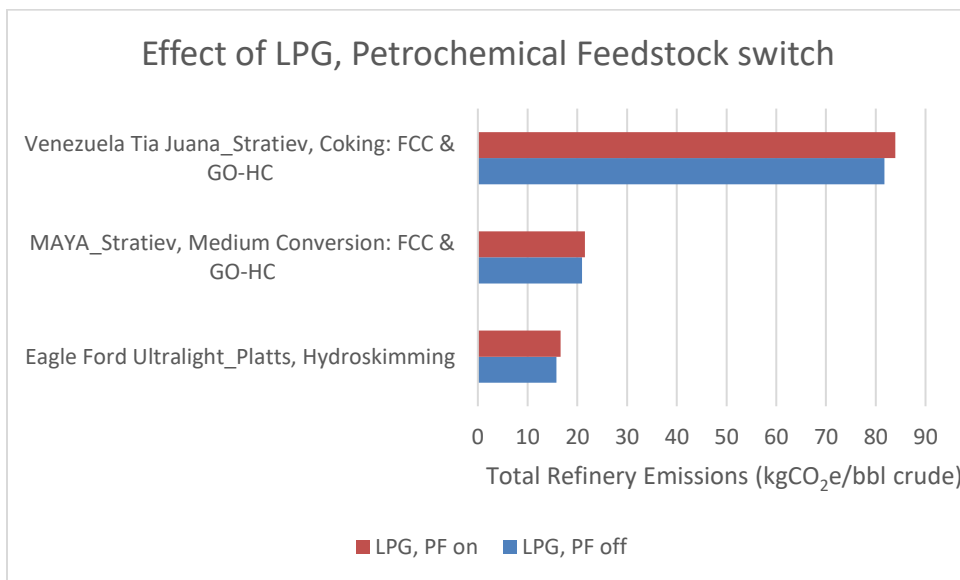
The greatest magnitude of change occurs from the deep conversion configuration compared to hydroskimming or medium conversion. This is due to larger amounts of off-gas production from the extra process units. Light crudes typically have the greatest percentage change in emissions, due to a high percentage of the light ends being suitable for LPG and petrochemical feedstock production.

Overall, refinery GHG emissions see an increase for light/medium crudes, and a decrease for heavy crudes due to inclusion of asphalt, LPG, and petrochemical production within PRELIM v1.1. This is consistent with the following observations:

- Asphalt production derives from the vacuum residue crude oil fraction. Asphalt production decreases total refinery GHG emissions for deep conversion configurations only, where the asphalt would otherwise be vacuum residue that would feed the coker or residue hydrocracker. Emissions associated with vacuum residue coking or residue hydrocracking, and further processing are avoided. Notice that incremental production of light products from the heavy ends of the crude is avoided as well. Asphalt is not produced at all in the hydroskimming configuration. In the medium conversion configurations, vacuum residue is not processed; thus, asphalt production does not change the amount of processing of the vacuum residue.
- LPG and petrochemical feedstock production increase total refinery GHG emissions for all configurations because of less available RFG; therefore, more natural gas is required to meet the refinery fuel demand. The increase in emissions is due to natural gas associated upstream emissions. Combustion emissions remain constant.
- For heavy crudes processed in deep conversion configurations, the emissions decrease from asphalt production is more significant than the increase from petrochemical feedstock production, resulting in a net decrease in refinery emissions.
- Light and medium crudes, processed in hydroskimming and medium conversion configurations respectively, see an increase in refinery emissions.

Implications of using hydroskimming configuration as a default for light crude oils

Default refinery configuration for light crudes is set following initial development of PRELIM (i.e., refinery configuration is defined by API and sulphur content of the crude). For the most part, light crude oils are sent to be refined in PRELIM hydroskimming refinery configuration. However, 74% of global refinery capacity is composed of medium and deep refining conversion infrastructure. In addition, light crude oil and products derived from topping and hydroskimming light crude processing are for the most part traded within refineries to be part of medium and deep conversion refinery crude slate feedstock in order to balance market demand and optimize the use of different processing unit capacities. Thus, the probability of light crudes to go through simple refining processing is the lowest. The assumption of limited processing of light crudes has a direct impact in the life cycle or well-known carbon intensity (CI) values assigned to these crudes: it impacts refinery emission estimates and downstream combustion emissions associated with the end use of the light crudes derived products. The impact

of such assumptions in the refinery emission estimates and the CI values for a crude compared to an alternative full processing refining scenario is evaluated in this section.

PRELIM v1.1 was used to run 3 different light crude processing scenarios:

1. PRELIM default pathway (Default): Light crudes run in PRELIM Hydroskimming configuration.
2. Most Probable Full Processing Refining pathway (New Scenario): Light crudes run in PRELIM Hydroskimming configuration, Hydroskimming fuel oil and heavy end oil products are transported and then processed in medium and deep conversion process units; Hydroskimming fuel oil and heavy end oil products are supplied directly into those processing units.
3. Alternative modeling approach for the "New Scenario" (Deep Conv+Extra T): Light crudes run through deep conversion refinery as a proxy of a Hydroskimming plus deep conversion refinery scenario, and the extra transportation associated with transporting PRELIM Hydroskimming fuel oil and heavy end oil products is added to pathway.

Other PRELIM default values were kept constant including the Global Warming potential AR5 without climate-carbon feedback factors chosen in PRELIM v1.1 and LPG option on. Emission factors for crude upstream production as estimated by the Oil Production Greenhouse Gas Emissions Estimator (OPGEE) life cycle tool, end products' transportation, and downstream/combustion were also considered. Impacts on the crude CI value were estimated for the Asphalt/Petrochemicals off scenario.

The CI values for light crude oils – GHG emissions per barrel of crude refinery gate to end use – has important changes for some crudes between the default simple processing pathway and the most probable full processing refining scenario (New Scenario). The magnitude of the deviation in these CIs ranges from 0.03% to 11.41%, and average 6.45% for PRELIM v1.1 assay inventory. The lowest impact is shown for the Algerian Condensate_BP crude assay, and it is related to the lack of vacuum residue in its distillation curve. The highest impact is shown for Nigeria Escravos_Chevron crude assay. For the Nigeria Escravos_Chevron crude assay, the downstream emissions increase by 0.4%, transportation emissions increase by 60%, and refining emissions increase by 465%; 53% of the increase in refining emissions is associated with hydrogen supply. The overall CI values – Well to Wheel – increase by 8.8%. Figure 33 illustrates the type of impact of the assumption on refining scenario for the crudes CI emission estimates: No impact, average impact, and major impact.
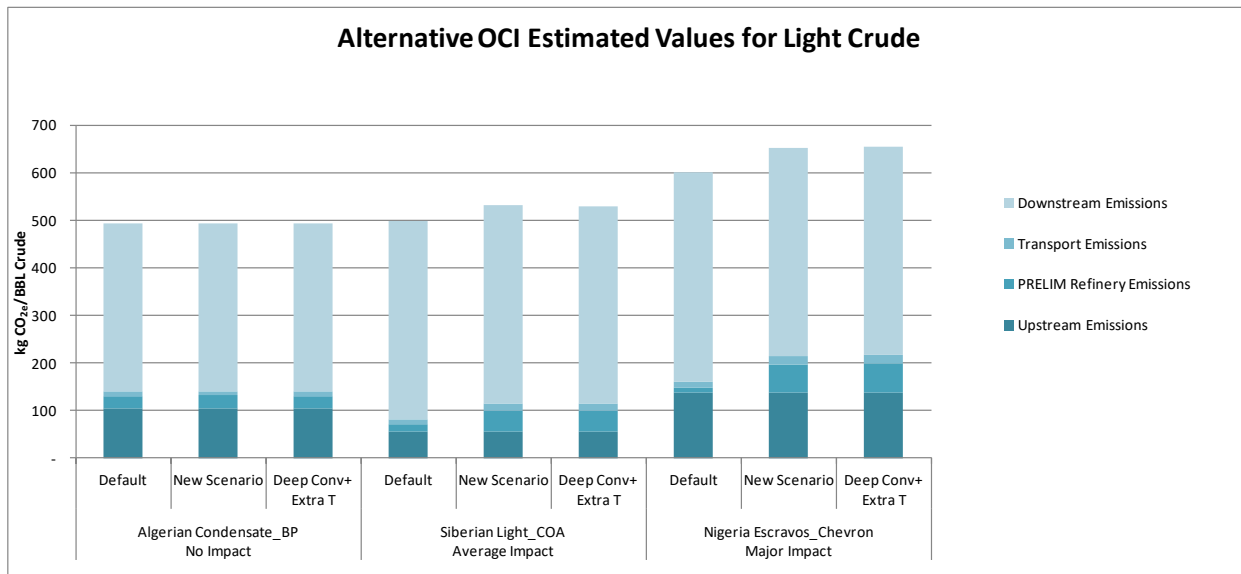
Figure 33 Impact of refinery pathway on crude carbon intensity estimated emission values.

Within PRELIM light crude oil assay inventory set to default as hydroskimming processing, the new scenario show:

- Downstream emissions to deviate in a range of -3.50 to 0.28%, and average of 1.06%.
- Transport emissions to deviate in a range of 0.31% to 60.4%, and average of 40.5%.
- Refining emissions to deviate in a range of 0.61% to 465%, and average 200%.
- CI values that include upstream emissions estimates to deviate in a range of 0.02% to 8.8%. For Wyoming Sweet_COA crude assay with lowest OPGEE upstream emissions estimates, CI value deviate 6.0%.

PRELIM users may use the deep conversion refinery scenario as a proxy of the potential emissions that result in a light crude full processing scenario. However, the users should be aware that an increase in emissions will be expected mainly because of changes in refinery processing efficiencies. Also, on a life cycle basis, changes will result from additional transportation related to movement of intermediate and final products. Table illustrates life cycle emission estimates for three different crudes in the default hydroskimming scenario, the New Scenario, the Deep Conversion scenario, and a Deep Conversion scenario that includes an extra transportation associated with transporting Hydroskimming fuel oil and heavy end oil products as a proxy for the new scenario.

Table 14 Carbon Intensity values for light crudes: PRELIM default and full conversion

Life Cycle Stages	Wyoming Sweet_COA				Sumatran Light (Minas)_Chevron				Nigeria Escravos_Chevron			
	Default	New Scenario	Deep Conv	Deep Conv+ Extra T	Default	New Scenario	Deep Conv	Deep Conv+ Extra T	Default	New Scenario	Deep Conv	Deep Conv+ Extra T
Upstream Emissions	67.97	67.97	67.97	67.97	254.14	254.14	254.14	254.14	138.94	138.94	138.94	138.94
PRELIM Refinery Emissions	16.15	45.09	46.54	46.54	9.58	48.95	45.02	45.02	10.22	57.78	59.22	59.22
Transport Emissions	10.61	15.03	10.26	15.03	10.76	17.11	10.25	17.09	11.18	17.94	10.69	17.93
Downstream Emissions	424.91	422.86	422.70	422.70	434.91	422.45	421.76	421.76	439.30	437.55	437.27	437.27
Total	519.64	550.95	547.47	552.24	709.39	742.65	731.17	738.01	599.64	652.20	646.12	653.37
Relative deviation		6%	-0.6%	1%		5%	-2%	1%		9%	-0.9%	1%

The results confirm that deep conversion scenario values can be used as a proxy of well to wheels full conversion refining scenario of light crudes (i.e. deviation between New Scenario and Deep Conversion emissions is less than 1%). The proxy can be improved by incorporating associated additional transportation emissions (i.e., deviation reduces to less than 0.6%). However, the results also show that in order to evaluate emission mitigation options, details about each crude at each life cycle stage should be considered; more detailed modeling is needed as the one use for the "New Scenario". For example, at a system level, for some crudes, there may be inefficiencies in processing the crude in two different refinery facilities while for others it is not the case. In this modeling exercise, it was found that crude specific refinery hydrogen balance factors in whether the deep conversion scenario is or is not a good proxy for determining emissions associated with full processing of light crudes through the topping/ hydroskimming refining and subsequent deep conversion pathway. Crudes that can supply excess of hydrogen during simple refining will only obtain credit in the deep conversion scenario/proxy modelling as opposed to in the "New Scenario"/detailed modeling. Table 15 shows the deviation in refinery emission estimates between detailed modeling and the proxy for the crudes with surplus of hydrogen in simple refining processing.

Table 15 Deviation in refinery emission estimates between "New Scenario"/detailed modeling and deep conversion for crudes with surplus of hydrogen in Hydroskimming configuration.

Crude Assay	Deviation in refinery emissions	Crude Assay	Deviation in refinery emissions
Nigeria Agbami_Chevron	22.34%	Nigeria Pennington_Chevron	6.14%
West Texas Intermediate_Statiev	5.64%	Nigeria Escravos_Chevron	-2.44%
Nanhai Light_Chevron	15.91%	Ekofisk_Chevron	4.13%
Nigera Quaib_Exxon	5.46%	Cossack_Chevron	9.25%
Siberian Light_COA	4.19%	Brent_Chevron	5.98%
Sumatran Light (Minas)_Chevron	8.72%	Azeri Light_Chevron	10.61%

As illustrated, the implications outlined in this section for PRELIM default configurations are specific for each crude and will be defined by market development. For example, notice PRELIM v.1.1 includes assays to represent Tight oil condensate crude. Like other light sweet crudes, the assays are assumed to be processed by default in the hydroskimming configuration. However, the user should be aware than on a life cycle basis these crudes have shown to be blended directly with other crudes either as diluent or as a refinery feedstock. They also have been used as a petrochemical feedstock. The level of processing for these crudes starts from either the use of stabilizers in the production field that split the crude into a single top and bottom stream to remove the light end components that make a stream "unstable" and prepare the stream for transport" or the use of splitters that split the crude into several streams (i.e., an overhead stream that contains LPGs and lighter components and some light naphtha material, a full-range naphtha and distillate fractions that would be taken off as individual side cuts, and the bottoms stream that would contain the remaining gas oils and heavier components). The fate of these types of crudes will depend of how many stabilizers versus splitter projects are implemented within U.S. to allocate their materials in the market. The use of PRELIM to model different processing scenarios will be impacted by the different factors outlined here for other light crudes and the magnitude of the impacts must be evaluated for different processing scenarios.

Buyers of processed US condensate are purchasing to feed splitters and blend with crude

Buyers	Seller	Cargo (kbbl)	Comments
GS Caltex	Enterprise Products	400	GS Caltex does not have a splitter and is reportedly sourcing condensate to blend with crude
COSMO	Enterprise Products	300	Purchased at US$4/bbl discount to Middle Eastern grades; sourced for crude blending at Yokkaichi refinery
SK innovation		400	For splitter at Incheon petrochemical complex or for blending with crude at Ulsan refinery
Vitol	bhpbilliton		BHP Billiton loaded its first export cargo to Vitol; Vitol has reportedly been selling to France
KOCH	bhpbilliton	650	Koch owns a splitter in Rotterdam
MITSUBISHI	Enterprise Products	600	Petro-Diamond Singapore, the oil trading subsidiary of Mitsubishi Corporation, signed a long-term agreement with Enterprise for 2015

Source: Press search   EnergyInsights |

U.S. condensate purchased to feed splitters and blend with crude

Source: McKinsey Solutions, 2015.

Minor Changes

- Heating values that are used to calculate total MJ/d of product now correspond to dynamically calculated heating values, calculated from final product properties on `HydroRefineryPFD` and `HydroRefineryPFD` sheets.

Corrections

- Correction to excel code used for presentation of "Bunker C" now "Light Heavy Ends" values in PRELIM v1.0 cells D123, D132, and D145 on the `Results Single Assay` worksheet (i.e., cells D132, D141, and D157 in the new version PRELIM V1.1):
  - Although the excel code that determine the values to be shown in these cells had to be corrected (only for display of results), correct values were already being used in the calculations of the model. Therefore, the abovementioned cells are the only part of the model affected due to this correction.
- Correction to calculation of hydrogen content of the gasoline, value presented in PRELIM v1.0 cell D32 on the `Results Single Assay` worksheet (i.e., cell D35 in the new version PRELIM V1.1):
  - This error was a calculation error when the `SRNaphtha+Heavy naphtha` option was selected from the `Naphtha catalytic reformer feed` options dropdown menu on the "`Main Input & Output`" worksheet in PRELIM v1.0. The correction only changed the value reported for the gasoline hydrogen content on the `Results Single Assay` worksheet, and it only occurred when a crude assay was run the coking deep conversion and the abovementioned `Naphtha catalytic reformer feed` option was selected. In PRELIM, the result is provided for information purposes, and there are not impacts of dependent formulas/calculations to this value. Thus, no other results are affected by the correction (i.e., the error did not affect energy or GHG emissions estimates). The result only affects users' use of this parameter.

- Correction to excel code used for presentation of Surplus of refinery fuel gas values in PRELIM v1.0 cells D19, D28, D124, and D133 on the `Results Single Assay` worksheet (i.e., cells D19, D28, D133 and D142 in the new version PRELIM V1.1):
  - The displayed result was surplus of refinery fuel gas as heating fuel before accounting for its use for steam and hydrogen supply.
  - Although the excel code that determine the values to be shown in these cells had to be corrected (only for display of results), correct values were already being used in the calculations of the model. Therefore, the abovementioned cells are the only part of the model affected due to this correction.
- Correction to assumption on Kw for delayed cooking gas oil from 12 to 11.5 in the `CokingRefineryCalcs` and `HydroRefineryCalcs` worksheets. The change does not impact previous version of PRELIM as the assay inventory was narrow and the input to hydrocracking and FCC units remain within the process unit yield curves data.

Changes and Updates from PRELIM model published in 2012 to PRELIM v.1.0

Minor modifications were made between PRELIM v.1.0 and model published in 2012 to improve PRELIM accuracy, flexibility, and the number of crudes that were included in the model. The modifications result in slight variations in the results for similar crude assays run in PRELIM v.1.0 compared with the publication using the 2012 version of PRELIM (see Abella and Bergerson, 2012). The following are the largest two changes that were made:

1) Change to naphtha hydrotreater calculations:

Utility (steam and electricity) requirements in the naphtha hydrotreater unit were being consistently but slightly overestimated. This then resulted in slight inaccuracies in the hydrogen requirement that could be either over or underestimated. This modification is the reason behind the small differences between the results of emissions of the current version and the 2012 version of the model.

2) Change to hydrogen content of the output stream of the hydrotreaters:

PRELIM uses a default output hydrogen content value for the hydrotreaters to which the hydrogen content of the input stream has to be increased. In the 2012 version of the model, if the input stream to a hydrotreater has a hydrogen content higher than the default output hydrogen content, a negative hydrogen requirement results for that hydrotreater. This can translate to less total hydrogen required than what would have to be met by the SMR unit). PRELIM v1.0 included mass balance equations to adjust the default output hydrogen content value to a value that brings the otherwise negative hydrogen requirement of the hydrotreater to zero. This change was applied in the model to make it flexible for investigation of some of the new assays that have been added to the model after 2012. This did not affect the crude assays run in the 2012 version of the model.

To assess the impact of the modifications to the model, the two models were run for the same assays that were presented in the 2012 publication. The main assumptions are copied below from the paper:

• Refining configuration is based on API and sulphur properties of the whole crude for both crude categories Conventional and OS-derived crudes: API (light API > 32, medium 32 > API > 22, heavy API <22) and sulphur content (S) (sweet S < 0.5 wt %, sour S > 0.5 wt %). Sweet light crudes (Sw, L) are run in a hydroskimming refinery; sour light (So, L), sweet medium (Sw, M), and sour medium (So, M) crudes are run in a medium conversion refinery; and heavy crudes (H: conventional, bitumen, dilbits) are run in a full conversion refinery.

- Upgrading process units for the medium conversion refinery include a fluid catalytic cracking (FCC) process unit, and upgrading process units for full/deep conversion refinery include FCC and delayed coking process units.

> Note: 1) These configurations correspond to configurations number 1 (medium conversion: FCC) and 4 (deep conversion: FCC) for medium and deep conversion configurations, respectively. In the current version of the model the configuration selector chooses configurations number 3 (medium conversion: FCC+GO-HC (gas oil hydrocracker)) and 6 (deep conversion: FCC+GO-HC) for the crudes that require medium and deep conversions, respectively. 2) Both the new and the 2012 versions of PRELIM report emissions in kgCO2/bbl of crude whereas the results in the 2012 paper have been reported in gCO2/MJ of crude. The emissions reported in kgCO2/bbl need to be converted (using conversion factors and enthalpy of the crudes) into gCO2/MJ of crude when comparing the results of the model with those reported in the 2012 paper (Abella and Bergerson, 2012).

For the comparison presented here, the percentage difference between the total emissions estimates of the two models was primarily considered. The fix in the naphtha hydrotreater calculations was the main source of the differences between the results of the two versions for all of the crudes in the set of the 2012 assays. The differences between the GHG emissions estimates obtained from the two models were mostly insignificant. The differences between the model results for crude assays presented in the 2012 publication are presented in Table 16.

Table 16: Comparison of emissions estimates in PRELIM v.1.0 and the PRELIM 2012 version

Assay Name	Notation	Refinery Configuration	PRELIM v.1.0 (gCO$_2$/MJ crude)	PRELIM 2012 (gCO$_2$/MJ crude)	Change % (new result with respect to old result)
Mixed Sweet Blend	Conv, Sw, L2	Hydroskimming(0)	2.96	3.22	-8.02
High Sour Edmonton	Conv, So, L2	Medium Conversion: FCC (1)	5.02	4.99	0.62
Midale	Conv, So, M1	Medium Conversion: FCC (1)	5.97	6.08	-1.78
Bow River North	Conv, So, H1	Deep Conversion: FCC(4)	11.19	10.66	4.97
Suncor Synthetic A	SCO, Sw, L2	Hydroskimming(0)	2.78	2.99	-7.03
Husky Synthetic Blend	SCO, Sw, L1	Hydroskimming(0)	2.09	2.20	-5.01
Syncrude Synthetic	SCO, Sw, M1	Medium Conversion: FCC (1)	9.11	9.13	-0.21
Suncor Synthetic H	SCO, So, H1	Deep Conversion: FCC (4)	16.42	15.79	3.95
Albian Heavy Synthetic	Syndilbit 1	Deep Conversion: FCC (4)	12.26	11.81	3.82
Cold Lake	Dilbit 2	Deep Conversion: FCC (4)	11.11	10.47	6.08
Confidential	Bitumen 2	Deep Conversion: FCC (4)	13.77	13.59	1.31

Assay Name	Notation	Refinery Configuration	PRELIM v.1.0 (gCO$_2$/MJ crude)	PRELIM 2012 (gCO$_2$/MJ crude)	Change % (new result with respect to old result)
Confidential	Bitumen 1	Deep Conversion: FCC (4)	13.90	13.40	3.74

*Table 17: Comparison of emissions estimates in PRELIM v.1.0 and the PRELIM 2012 version
(Table 9 results with units of kgCO$_2$/bbl of crude)*

Assay Name	Notation	Refinery Configuration	PRELIM v.1.0 (kgCO$_2$/bbl crude)	PRELIM 2012 (kgCO$_2$/bbl crude)	Change % (new result with respect to old result)
Mixed Sweet Blend	Conv, Sw, L2	Hydroskimming(0)	16.24	17.65	-8.02
High Sour Edmonton	Conv, So, L2	Medium Conversion: FCC (1)	27.93	27.76	0.62
Midale	Conv, So, M1	Medium Conversion: FCC (1)	34.18	34.80	-1.78
Bow River North	Conv, So, H1	Deep Conversion: FCC(4)	65.62	62.51	4.97
Suncor Synthetic A	SCO, Sw, L2	Hydroskimming(0)	15.51	16.69	-7.03
Husky Synthetic Blend	SCO, Sw, L1	Hydroskimming(0)	11.67	12.28	-5.01
Syncrude Synthetic	SCO, Sw, M1	Medium Conversion: FCC (1)	51.26	51.37	-0.21
Suncor Synthetic H	SCO, So, H1	Deep Conversion: FCC (4)	97.52	93.81	3.95
Albian Heavy Synthetic	Syndilbit 1	Deep Conversion: FCC (4)	72.60	69.93	3.82
Cold Lake	Dilbit 2	Deep Conversion: FCC (4)	64.45	60.76	6.08
Confidential	Bitumen 2	Deep Conversion: FCC (4)	84.05	82.96	1.31
Confidential	Bitumen 1	Deep Conversion: FCC (4)	86.32	83.20	3.74

The same results are presented with a breakdown of the contributions to the GHG emissions in Figure 34 (PRELIM v.1.0) and Figure 35 (PRELIM 2012).
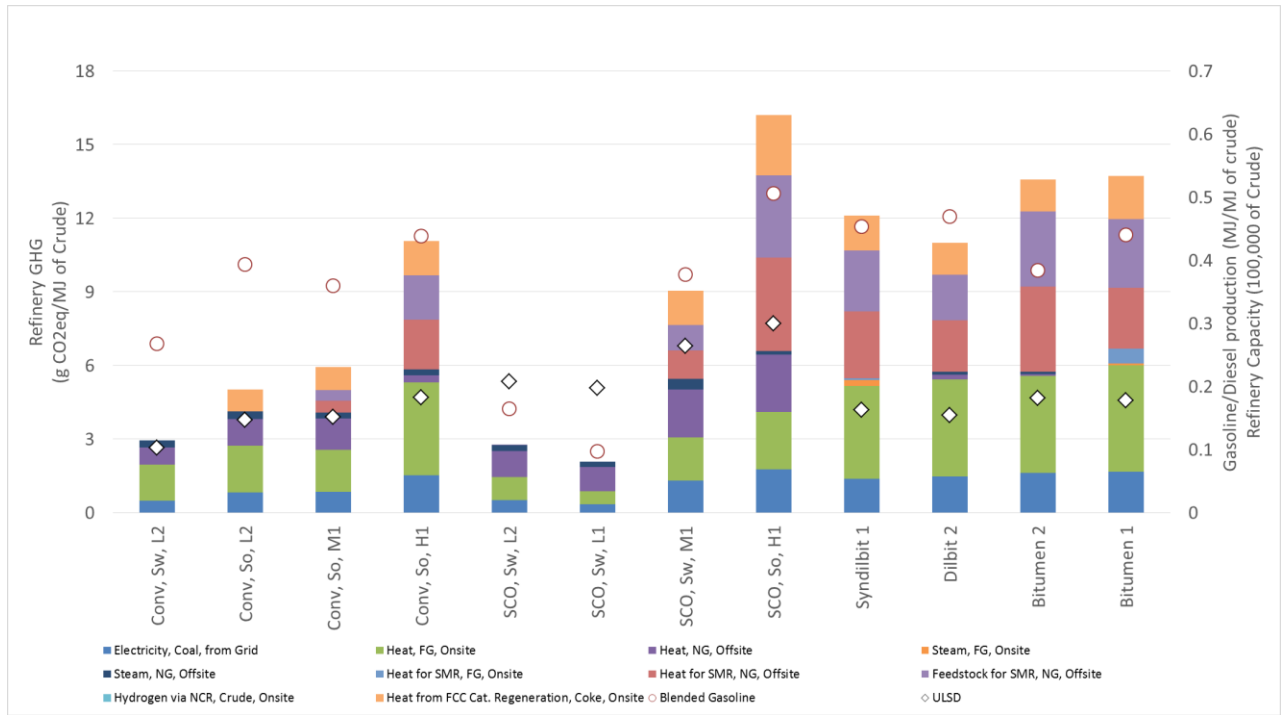
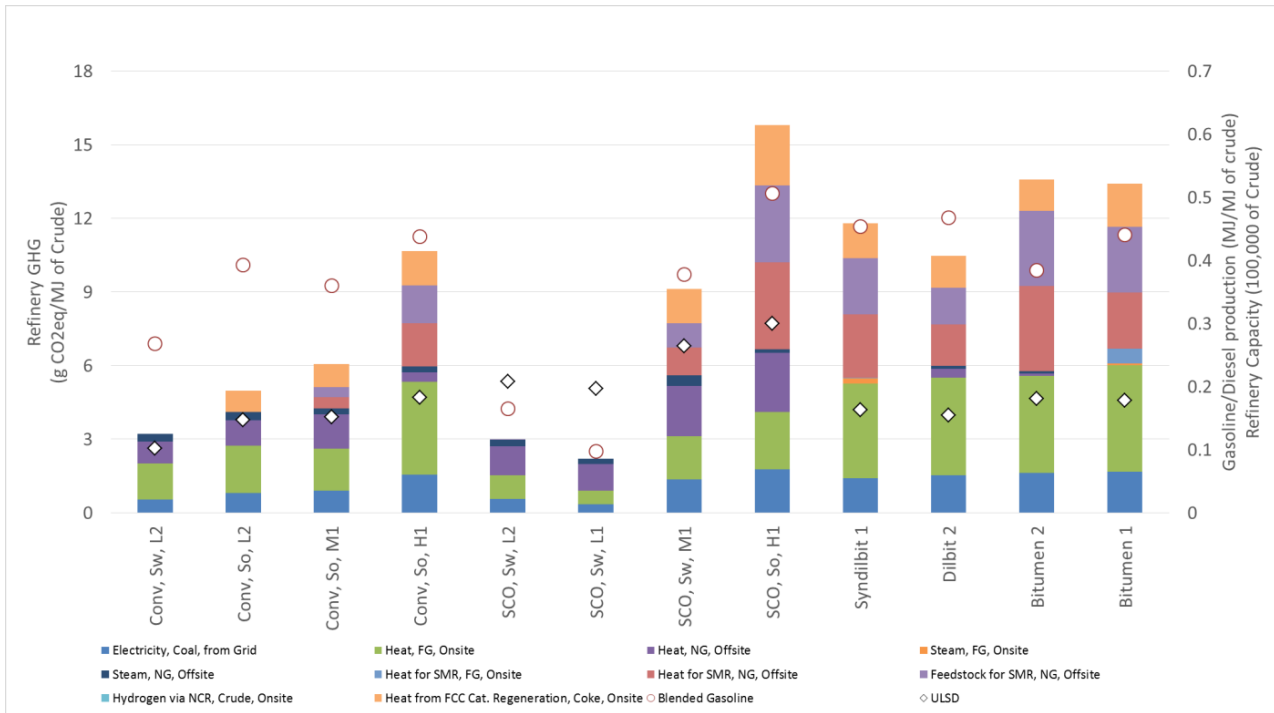*Figure 34: Breakdown of contributions to GHG emissions (results from PRELIM v.1.0)*

Figure 35: Breakdown of contributions to GHG emissions (results from PRELIM 2012)

Appendix B: References

B.1 References used in the documentation

Abella, J., Model to Investigate Energy and Greenhouse Gas Implications of Refining Petroleum, Masters Thesis, Department of Chemical and Petroleum Engineering, University of Calgary, Calgary, 2012.

Abella J.; Bergerson J., Model to Investigate Energy and Greenhouse Gas Emissions Implications of Refining Petroleum: Impacts of Crude Quality and Refinery Configuration in Environmental Science & Technology, 46, 13037-13047, 2012. URL: http://pubs.acs.org/doi/abs/10.1021/es3018682.

Argonne National Laboratory, Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation model GREET version 1.8 c.0. In May 2009 ed.; 2009.

Baird, C., Petroleum Refining Process Correlations. 1987, Austin, Texas: HPI Consultants.

Baker & O'Brien PRISM Overview. http://www.bakerobrien.com/services/PRISM (PRISM is a licensed trademark of Baker & O'Brien, Inc. All rights reserved).

Baumann, H.; Tillman, A.-M., The Hitch Hiker's Guide to LCA. An orientation in lifecycle assessment methodology and application. Studentlitteratur: Lund, Sweden, 2004.

Brierley, G.; Gembicki, V.; Cowa, T., Changing the refinery configuration for heavy and synthetic crude processing. In UOP LLC: Des Plaines, Illinois, USA, 2006; p 23.

Castañeda, L. C.; Muñoz, J. A. D.; Ancheyta, J., Comparison of approaches to determine hydrogen consumption during catalytic hydrotreating of oil fractions. Fuel, 2011.

Choudhary, T. V.; Meier, P. F., Characterization of heavy petroleum feedstocks. Fuel Processing Technology 2008, 89, (7), 697-703.

Ciroth, A. ICT for Environment in Life Cycle Applications OpenLCA, A New Open Source Software for Life Cycle Assessment. International Journal of Life Cycle Assessment, 2007, 12 (4), 209.

EIA Documentation for Emissions of Greenhouse Gases in the United States 2006. Chapter 6; U.S. Department of Energy, Energy Information Administration Office of Integrated Analysis and Forecasting October, 2008.

EIA, Refinery Capacity 2008. In U.S. Department of Energy, Energy Information Administration: 2008.

EIA, Ranking of U.S. Refineries. In September, 2010 ed.; U.S. Department of Energy, Energy Information Administration: 2010.

EIA, U.S. Number and Capacity of Petroleum Refineries. In June 25, 2010 ed.; U.S. Department of Energy, Energy Information Administration: 2010.

Energetics. Energy Bandwidth for Petroleum Refining Processes; Prepared by Energetics Incorporated for the U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Industrial Technologies: 2006; p 17.

Energetics. Energy and Environmental Profile of the US Petroleum Refining Industry Prepared by Energetics Incorporated Columbia, Maryland for U.S. Department of Energy Industrial Technologies Program: November 2007; pp 39, 40.

EPA. Catalog of CHP Technologies. U.S. Environmental Protection Agency: 2015. http://www.epa.gov/chp/documents/catalog_chptech_full.pdf.

EPA Inventory of U.S. Greenhouse Gas Emissions and Sinks:1990 – 2007 U.S. Environmental Protection Agency: April 15, 2009; pp 3-43.

Fahim, M.A., T.A. Alsahhaf, and A. Elkilani, Fundamentals of Petroleum Refining. 2010: Elsevier.

Gary, J.; Handwerk, G.; Kaiser, M., Petroleum Refining Technology and Economics Fifth ed.; CRC Press: New York, 2007.

Goossens, A. G., Prediction of Molecular Weight of Petroleum Fractions. Industrial & Engineering Chemistry Research 1996, 35, (3), 985-988.

Goossens, A. G., Prediction of the Hydrogen Content of Petroleum Fractions. Industrial & Engineering Chemistry Research 1997, 36, (6), 2500-2504.

Grover, B.; Di Zanno, P., Study examines use of refinery fuel gas for hydrogen production. Oil & Gas Journal 2007, 105, (24), 4.

Hassan, A.; Carbognai, L.; Sosa, C.; Trujillo, G.; Pereira-Almao, P. A Faster Set- up for the Estimation of Microcarbon Residue for Heavy Oil and Fractions, 2009.

Haverly Systems Inc. Haverly's Crude Assay Management System (H/CAMS). http://www.haverly.com/main-products/13-products/10-hcams (H/CAMS is a trade mark of Haverly Systems, Inc. All rights reserved).

IHS Energy Special report comparing GHG intensity of the oil sands and the average US crude oil, 2014.

Jacobs Consultancy (Jacobs). Life Cycle Assessment Comparison of North American and Imported Crudes. Alberta Energy Research Institute and Jacobs Consultancy, 2009.

Jones, D. S. J. S.; Pujadó, P. R.; Gruia, A., Hydrotreating. In Handbook of Petroleum Processing, Springer Netherlands: 2006; pp 321-354.

Jones, D. S. J., Refinery Gas Treating Processes. In Handbook of Petroleum Processing, Jones, D. S. J.; Pujadó, P. R., Eds. Springer: Netherlands 2008; pp 431-432. 120. SPEIGH, J. G., Chemistry and Technology of Petroleum. Marcel Dekker: New York, 1991.

Karpe, P., Refinery Utilities. ConocoPhillips. Personal Communication. In Abella, J., Ed. Calgary, 2010.

Krause, P.; Boyle, D. P.; Base, F., Comparison of different efficiency criteria for hydrological model assessment. Advances in Geosciences 2005, 5, 89-97.

Life Cycle Associates, LLC Assessment of direct and indirect GHG emissions associated with petroleum fuels, 2009.

Lloyd, S. M.; Ries, R., Characterizing, Propagating, and Analyzing Uncertainty in Life-Cycle Assessment: A Survey of Quantitative Approaches. Journal of Industrial Ecology 2007, 11, (1), 161-179.

McKinsey Solutions. Testing the waters: US condensates exports take off. Energy Insights. August 2015. https://www.mckinseyenergyinsights.com/insights/us-condensates-exports-take-off.aspx Press Search

Maples, R. E., Linear regression determines crude properties at variable boiling points. The Oil and Gas Journal 1997, v95, (n44), p72(2).

Maples, R., Petroleum Refinery Process Economics. . Second ed.; PennWell Corp: 2000.

Márquez-Riquelme, E. F.; van der Steen, J.; Balzer, C.; Maas, W., Accurate correlations to estimate refinery fuel gas, natural gas, and fuel oil CO2 emission factors and its uncertainty. AIChE Journal 2010, 56, (9), 2479-2488.

Mc.Ketta, J., Encyclopedia of Chemical Processing and Design. In p 309, 1993.

Moharam, H. M.; Braek, A. M.; Fahim, M. A., A Simple Method of Estimating the Enthalpy of Petroleum Fractions. Industrial & Engineering Chemistry Research 1998, 37, (12), 4898-4902.

Motazedi, K.; Abella, J.; Bergerson, J., Techno-economic Evaluation of Technologies to Mitigate Greenhouse Gas Emissions at North American Refineries in Environmental Science & Technology, 51, 1918-1928, 2017. URL: http://pubs.acs.org/doi/abs/10.1021/acs.est.6b04606.

Natural Resources Canada, GHGenius A model for life cycle assessment of transportation fuels. http://www.ghgenius.ca.

NETL. Development of Baseline Data and Analysis of Life Cycle Greenhouse Gas Emissions of Petroleum-Based Fuels DOE/NETL-2009/1346. National Energy Technology Laboratory: 2008.

NETL. An Evaluation of the Extraction, Transport and Refining of Imported Crude Oils and the Impact on Life Cycle Greenhouse Gas Emissions DOE/NETL-2009/1362. National Energy Technology Laboratory: 2009.

Parkash, S., Refining Processes Handbook. Elsevier: Burlington, 2003.

Riazi, M., Characterization and Properties of Petroleum Fractions. ASTM International Standards. . Baltimore, 2007.

Robinson, P. R., Hsu, C.; Petroleum Processing Overview. In Practical Advances in Petroleum Processing, Eds. Springer New York, 2006; Vol. 1, pp 14,15,18,21.

Skone, T.; Gerdes, K. Development of Baseline Data and Analysis of Life Cycle Greenhouse Gas Emissions of Petroleum-Based Fuels DOE/NETL-2009/1346; National Energy Technology Laboratory (NETL): November 26, 2008.

Smith, R. L.; Watson, K. M., Boiling Points and Critical Properties of Hydrocarbons. Industrial & Engineering Chemistry 1937, 29, (12), 1408-1414.

Spath, P. L.; Mann, M. K. Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming; NREL/TP-570-27637; National Renewable Energy Laboratory: 2001.

Stratiev, D.; Tzingov, T.; Shishkova, I.; Dermatova, P., Hydrotreating units chemical hydrogen consumption analysis: A tool for improving refinery hydrogen management. In 44th International Petroleum Conference, Bratislava, Slovak Republic, 2009.

Szklo, A.; Schaeffer, R., Fuel specification, energy consumption and CO2 emission in oil refineries. Energy 2007, 32, (7), 1075-1092.

Villalanti, D. C.; Raia, J. C.; Maynard, J. B., High-temperature Simulated Distillation Applications in Petroleum Characterization. In Encyclopedia of Analytical Chemistry, Meyers, R. A., Ed. Ó John Wiley & Sons Ltd: Chichester, 2000; pp 6726– 6741.

Wang, M.; Lee, H.; Molburg, J., Allocation of Energy Use in Petroleum Refineries to Petroleum Products. Implications for Life-Cycle Energy Use and Emission Inventory of Petroleum Transportation Fuels. The International Journal of Life Cycle Assessment 2004, 9, (1), 10.

Watson, K. M.; Nelson, E. F., Improved Methods for Approximating Critical and Thermal Properties of Petroleum Fractions. Industrial & Engineering Chemistry 1933, 25, (8), 880-887.

Wiley, J.; Sons, Part I Oil Refining, Environmental Considerations. In Wiley Critical Content: Petroleum Technology Wiley-Interscience: 2007; Vol. 1, pp 347-352. 78.

B.2 Other references used to build the model

Air Resources Board, Clean Final Regulation Order (Part 1 and 2) to Implement the Low Carbon Fuel Standard. In California Environmental Protection Agency, Ed. Sacramento, CA, 2009.

Alberta Innovates Life Cycle Analysis http://www.ai-ees.ca

Ancheyta, J.; Sánchez, S.; Rodríguez, M. A., Kinetic modeling of hydrocracking of heavy oil fractions: A review. Catalysis Today 2005, 109, (1-4), 76-92.

API Compendium of Greenhouse Gas Emissions Methodologies for the Oil and Gas Industry; American Petroleum Institute: 2004.

Argonne National Laboratory The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) Model. http://greet.es.anl.gov/

Aspen Technology Aspen Hysys Petroleum Refining. http://www.aspentech.com/products/aspen-refsys.aspx

Behrenbruch, P.; Dedigama, T., Classification and characterisation of crude oils based on distillation properties. Journal of Petroleum Science and Engineering 2007, 57, (1-2), 166-180.

Bellocchi, G.; Rivington, M.; Donatelli, M.; Matthews, K., Validation of biophysical models: issues and methodologies. A review. Agron. Sustain. Dev. 30, (1), 109-130.

Bergerson, J. A.; Lave, L. B., Baseload Coal Investment Decisions under Uncertain Carbon Legislation. Environmental Science & Technology 2007, 41, (10), 3431-3436.

Bevilacqua, M.; Braglia, M., Environmental efficiency analysis for ENI oil refineries. Journal of Cleaner Production 2002, 10, (1), 85-92.

Brandt, A. R. Upstream greenhouse gas (GHG) emissions from Canadian oil sands as a feedstock for European refineries; Department of Energy Resources Engineering. Stanford University: Stanford, 2011; pp 28, 29.

Bras-Klapwijk, R., Procedures and tools for generating and selecting alternatives in LCA. The International Journal of Life Cycle Assessment 2003, 8, (5), 266-272.

Bredeson, L.; Quinceno-Gonzalez, R.; Riera-Palou, X.; Harrison, A., Factors driving refinery CO2 intensity, with allocation into products. The International Journal of Life Cycle Assessment 2010, 15, (8), 10.

California Air Resources Board: Sacramento, C., 2009; www.arb.ca.gov/fuels/lcfs/workgroups/workgroups.htm#pathways. Detailed CA-GREET pathway for ultra low sulphur diesel (ULSD) from average crude refined in California, Version 2.1; California Air Resources Board: Sacramento, CA., 2009.

CA-LCFS Workgroup, Dertermining Carbon Intensity Values for Fuels Derived from Crude Oil. In California Air Resources Board: California, 2011.

CA-LCFS-Advisory-Panel, Low Carbon Fuel Standard Advisory Panel Draft Workplan Version 2. In California Air Resources Board: California, 2011.

Choquette-Levy, N. Should Alberta Upgrade Oil Sands Bitumen? An Integrated Life Cycle Framework to Evaluate Energy Systems Investment Tradeoffs. University of Calgary, Calgary, 2011.

Craig, E.; Unnasch, S.; Lowell, D.; (Acurex Corporation) The effect of Fuel Cycle Energy Efficiency and Transportation Efficiency on Greenhouse Gas Emissions; Prepared for the California Energy Commision: Sacramento, California, March 1991.

Crudemonitor.ca program, Canadian Crude Quality Monitoring Program http://www.crudemonitor.ca. In Monthly, Crude Quality Inc.The crudemonitor.ca program operates under a support model representing key stakeholders across the industry including the Canadian Association of Petroleum Producers (CAPP) and Small Explorers and Producers Association of Canada (SEPAC). 2010.

Delucchi, M. A Lifecycle Emissions Model (LEM): Lifecycle Emissions from Transportation Fuels, Motor Vehicles, Transportation Modes, Electricity Use, Heating and Cooking Fuels, and Materials; Institute of Transportation Studies. University of California, Davis: 2003.

Delucchi, M. Emissions of greenhouse gases from the use of transportation fuels and electricity; Argonne National Laboratory and Institute of Transportation Studies, University of California, Davis: 1993.

Ekelund, M. In Bitumen Markets & Economics, National Energy Board: Energy Futures 2010, Ottawa, 2010; Canada National Energy Board: Ottawa, 2010.

EIA International Energy Outlook 2011; DOE/EIA-08484; U.S. Department of Energy, Energy Information Administration: Washington, D.C., 2011; pp 2,119.

EIA, Petroleum and Other Liquids: Imports/Exports & Movements. In March, 2011 ed.; U.S. Department of Energy, Energy Information Administration: 2011.

EIA, International Energy Statistics. In U.S. Department of Energy, Energy Information Administration: Washington, D.C., 2011.

EIA, Canada Energy Data, Statistics and Analysis - Oil, Gas, Electricity, Coal. In Country Analysis Briefs: Canada, April 2011 ed.; U.S. Department of Energy, Energy Information Administration: 2011.

EIA, Petroleum and Other Liquids:Refinery Yield. In July 28 2011 ed.; U.S. Department of Energy, Energy Information Administration: 2011.

EPA Available and Emerging Technologies for Reducing Greenhouse Gas Emissions from the Petroleum Industry; U.S. Environmental Protection Agency: North Caroline, 2010.

EPA Climate Change - Regulatory Initiatives. http://www.epa.gov/climatechange/initiatives/index.html

EPA Renewable Fuel Standard (RFS). http://www.epa.gov/otaq/fuels/renewablefuels/index.htm

EPA, U.S. Greenhouse Gas Inventory. In August 2011 ed.; 2011.

EPA, Technical Support Document for the Petroleum Refining Sector: Proposed Rule for Mandatory Reporting of Greenhouse Gases. In U.S. Environmental Protection Agency, O. o. A. a. R., Ed. 2008.

Elizalde, I.; Rodríguez, M. A.; Ancheyta, J., Application of continuous kinetic lumping modeling to moderate hydrocracking of heavy oil. Applied Catalysis A: General 2009, 365, (2), 237-242.

Elizalde, I.; Rodríguez, M. A.; Ancheyta, J., Modeling the effect of pressure and temperature on the hydrocracking of heavy crude oil by the continuous kinetic lumping approach. Applied Catalysis A: General 2010, 382, (2), 205-212.

European Parliament and the Council of the European Union, amending Directive 98/70/EC as regards the specification of petrol, diesel and gas-oil and introducing a mechanism to monitor and reduce greenhouse gas emissions and amending Council Directive 1999/32/EC as regards the specification of fuel used by inland waterway vessels and repealing Directive 93/12/EEC In Official Journal of the European Union: 2009.

Gale, J., Sources of CO2. In Carbon Dioxide Capture and Storage. Intergovernmental Panel on Climate Change., Metz, B., Davidson, O., de Coninck, H., Loos, M., Meyer, L. , Ed. Cambridge University Press: New York, 2005; pp 75–104.

Gerdes, K.; Skone, T. An Evaluation of the Extraction, Transport and Refining of Imported Crude Oils and the Impact on Life Cycle Greenhouse Gas Emissions; National Energy Technology Laboratory (NETL): March 27 2009, 2009.

Giavarini, C.; Maccioni, F.; Santarelli, M. L., CO2 sequestration from coal fired power plants. Fuel 89, (3), 623-628.

Gunaseelan, P.; Buehler, C.; Chan, W. R., Greenhouse gas emissions: Characterization and management. Hydrocarbon Processing 2009, 88, (9), 57-70.

Hocking, D., MEG Energy. Personal Communication In Abella, J., Ed. Calgary, 2009.

Höjer, M.; Ahlroth, S.; Dreborg, K.-H.; Ekvall, T.; Finnveden, G. r.; Hjelm, O.; Hochschorner, E.; Nilsson, M. n.; Palm, V., Scenarios in selected tools for environmental systems analysis. Journal of Cleaner Production 2008, 16, (18), 1958-1970.

Fisher, I.P., Effect of feedstock variability on catalytic cracking yields. Applied Catalysis 1990, 65, (2), 189-210.

ISO, International Standard ISO 14041: Environmental management - Life cycle assessment - Goal and scope definition and inventory analysis. In for Standardization, I. O., Ed. Geneva, Switzerland, 1998.

Jacobs Consultancy Life Cycle Associates Life Cycle Assessment Comparison of North America and Imported Crudes; 2009.

Jiménez-González, C.; Overcash, M., Life Cycle Inventory of Refinery Products: A Review and Comparison of Commercially Available Databases. Environmental Science & Technology 2000, 34, (22), 4789-4796.

Karras, G., Combustion Emissions from Refining Lower Quality Oil: What Is the Global Warming Potential? Environmental Science & Technology 2010, null-null.

Katzer, J.; Ramage, M.; Sapre, A., Petroleum Refining: Poised for Profound Changes. Chem. Eng. Process 2000, 41-51.

Marano, J. J., GHG profiles for distillate fuels produced from conventional petroleum, oil sands, shale oil and XtL. Energy Procedia 2009, 1, (1), 3795-3799.

Marano, J. Investment Expectations & Decision Making In the Petroleum Refining Industry; DOE/EIA: 2007.

McCann, T.; Magee, P., Crude Oil Greenhouse Gas Life Cycle Analysis Helps Assign Values for CO2 Emissions Trading. The Oil and Gas Journal 1999, 97, (8), 38(1). 32. McCann, T.; ltd., A., Typical Heavy Crude and Derivative Greenhouse Life Cycles in 2007. In 2001.

Mertes, F.; Hurwicz, H.; (TRW Inc.) Energy Balances in the Production and End Use of Methanol Derived from Coal; U.S. Department of Energy: December, 1980.

Ministry of Energy and Mines, Renewable & Low Carbon Fuel Requirements Regulation, URL: http://www.em.gov.bc.ca/RET/RLCFRR.

National Renewable Energy Laboratory (NREL), Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming, URL: https://www.nrel.gov/docs/fy01osti/27637.pdf

O'Connor, D.; (S&T)2 Consultants Inc., GHGenius version 3.15. In May 2009 ed.; Natural Resource Canada's 2009.

Palou-Rivera, I.; Wang, M. Updated Estimation of Energy Efficiencies of U.S. Petroleum Refineries; Center for transportation Research. Argonne National Laboratory: 2010.

Peña-Díez, J. L., Improving Refinery Planning Through Better Crude Quality Control. In Practical Advances in Petroleum Processing, Hsu, C. S.; Robinson, P. R., Eds. Springer: New York, 2006; Vol. 1.

Rebitzer, G.; Ekvall, T.; Frischknecht, R.; Hunkeler, D.; Norris, G.; Rydberg, T.; Schmidt, W. P.; Suh, S.;

Weidema, B. P.; Pennington, D. W., Life cycle assessment: Part 1: Framework, goal and scope definition, inventory analysis, and applications. Environment International 2004, 30, (5), 701-720.

Rebitzer, G., Enhancing the Application Efficiency of Life Cycle Assessment for Industrial Use. École polytechnique fédérale de Lausanne, Berlin, Germany, 2005.

(S&T)2 Consultants Inc. Documentation for Natural Resources Canada's GHGenius Model 3.0; Delta, B.C., 2005.

(S&T)2 Consultants Inc. Crude Oil Production Update for GHGenius; Delta, B.C, 2007.

Schremp, G., Results of Initial Screening Process to Identify Potential HCICOs. In Crude Oil Screening - General Meeting, Commission, C. E., Ed. California Air Resources Board: 2011.

Self, F. E.; Ekholm, E.; Bowers, K. E., Characteristics of Petroleum Products. In Refining Overview—Petroleum, Processes, & Products, American Institute of Chemical Engineers AIChE: Texas, 2000.

Speight, J. G., Chemistry and Technology of Petroleum (3rd Edition). Marcel Dekker: New York, NY, USA, 1999.

Speight, J. G., Handbook of Petroleum Product Analysis. John Wiley & Sons: 2002.

Speight, J. G., Use of the Data - Mapping and Predictability. In Handbook of Petroleum Analysis, John Wiley & Sons: 2001.

Sword, L., Refinery Investments Align With Oil Sands Supplies to 2015. Oil & Gas Journal 2008, 106, (31), 4.

The Pembina Institute; University of Calgary; DuVair, P. Life Cycle Analysis of North American and Imported Crude Oils. Post-Workshop: Stakeholder Input; 2009.

TIAX LCC; MathPro Inc. Comparison of North America and Imported Crude Oil Life Cycle GHG Emissions; 2009.

van Straelen, J.; Geuzebroek, F.; Goodchild, N.; Protopapas, G.; Mahony, L., CO2 capture for refineries, a practical approach. International Journal of Greenhouse Gas Control 4, (2), 316-320.

Venkatesh, A.; Jaramillo, P.; Griffin, W. M.; Matthews, H. S., Uncertainty Analysis of Life Cycle Greenhouse Gas Emissions from Petroleum-Based Fuels and Impacts on Low Carbon Fuel Policies. Environmental Science & Technology 45, (1), 125-131.

Wang, M. GREET 1.5 — Transportation Fuel-Cycle Model, Vol 1: Methodology, Development, Use, and Results; Center for Transportation Research, Argonne National Laboratory: 1999.

Wang, F.; Rob, K.; Nigel, T., Factor Analysis and Principal-Components Analysis. In International Encyclopedia of Human Geography, Elsevier: Oxford, 2009; pp 1-7.

Weidema, B. P.; Wesnæs, M. S., Data quality management for life cycle inventories--an example of using data quality indicators. Journal of Cleaner Production 1996, 4, (3-4), 167-174.

Wise, T., Markets evolving for oil sands bitumen, synthetic crude. Oil & Gas Journal 2008, 106, (25), 6.

Worrell, E.; Galitsky, C. Energy efficiency improvement and cost saving opportunities for petroleum refineries; LBNL-56183; Ernest Orlando Lawrence Berkeley National Laboratory: 2005; pp 10-16.

Young, B.; Hottle, T.; Hawkins, T.; Jamieson, M.; Cooney, G.; Motazedi, K.; Bergerson, J., Expansion of the Petroleum Refinery Life Cycle Inventory Model to Support Characterization of a Full Suite of Commonly Tracked Impact Potentials. Environmental Science & Technology, 2019, 53 (4), 2238-2248.