

Supporting Information for

**Development and Application of a Life Cycle-based
Model to Evaluate Greenhouse Gas Emissions of Oil
Sands Upgrading Technologies**

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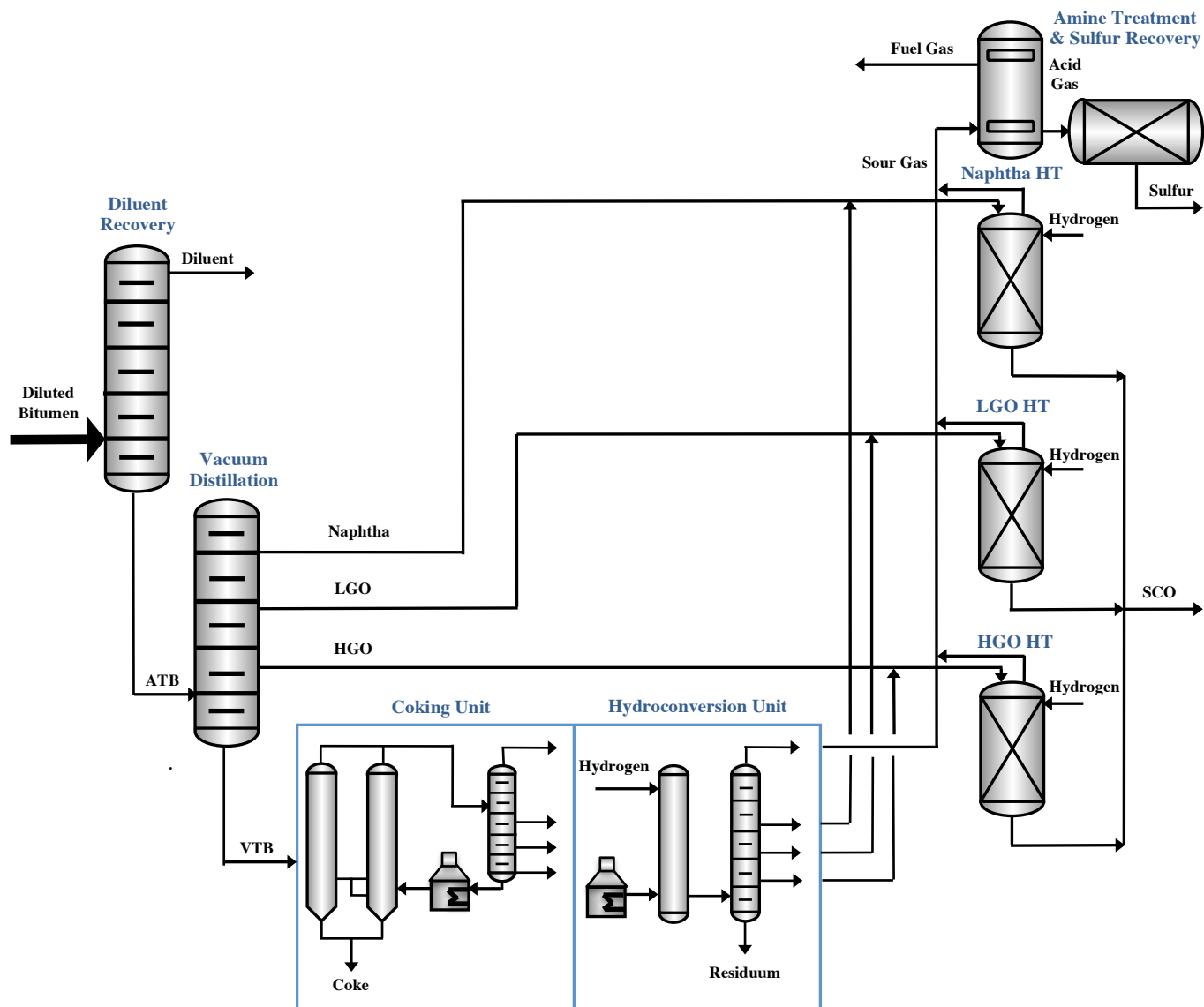
75 pages, 13 tables, 6 figures, 3 schemes

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Flowcharts: OSTUM's Upgrading Process Flow Diagram

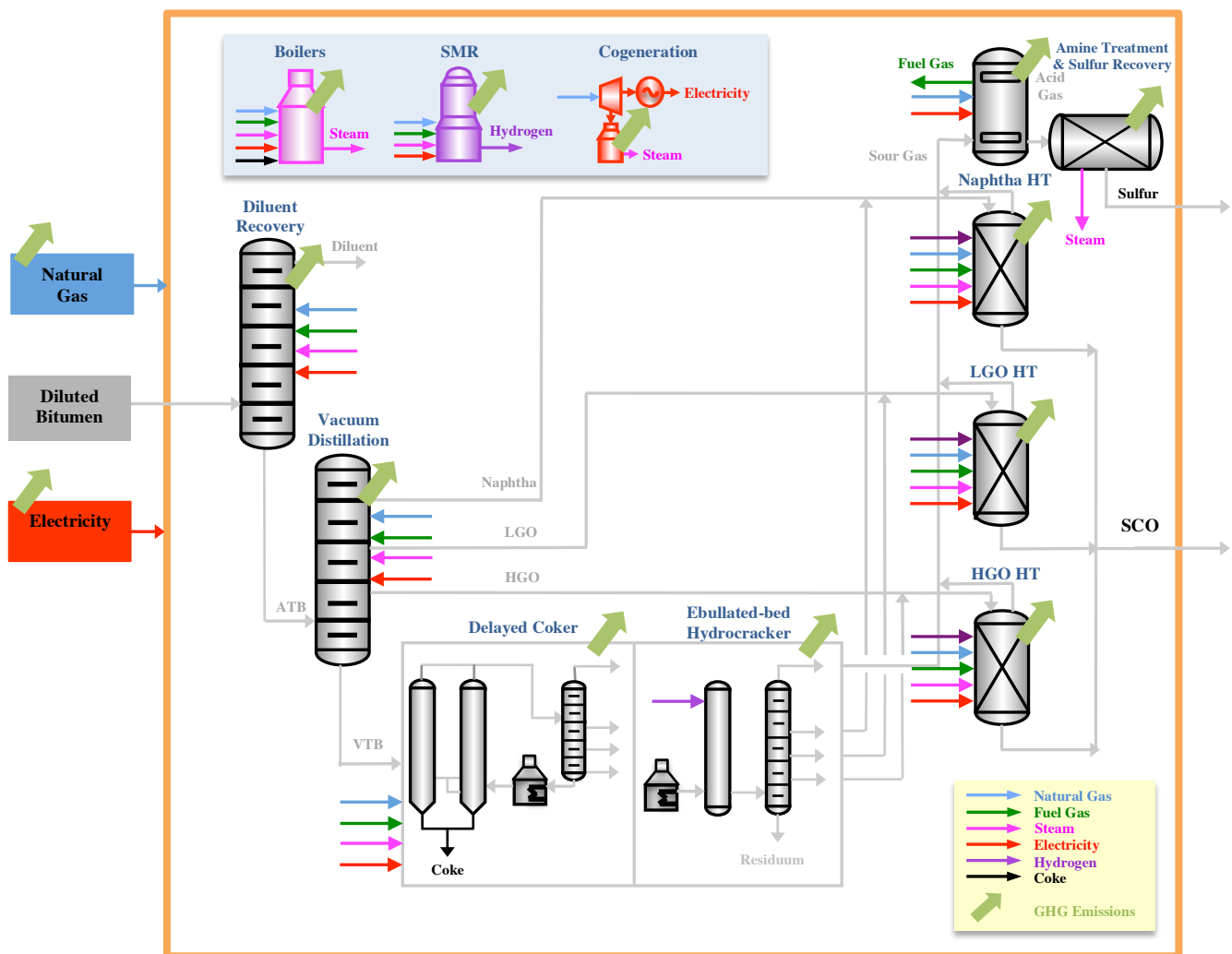
In OSTUM, its upgrading process starts with a diluent recovery unit (DRU) that separates the diluent from the diluted bitumen and recycles it to the production plant. The atmospheric-topped bitumen (ATB) is then processed in a vacuum distillation unit, which separates it into naphtha, light gas oil (LGO), heavy gas oil (HGO), and vacuum-topped bitumen (VTB). The VTB is then fed to a conversion unit: a delayed coker or an ebullated-bed hydrocracker, or a combination of both. Liquid product from the conversion unit is separated into naphtha, LGO and HGO through fractionation. Each fraction is combined with a similar one previously produced by vacuum distillation and directed to the corresponding naphtha, LGO or HGO hydrotreater ¹. The resulting hydrotreated liquids are blended to form synthetic crude oil (SCO). The ebullated-bed hydrocracker and HTs consume hydrogen. The delayed coker, ebullated-bed hydrocracker and HTs produce sour gas that is fed to an amine treatment unit for hydrogen sulfide (acid gas) removal. The resulting fuel gas is used as fuel in process furnaces. A sulfur recovery unit converts the sulfur contained in the removed acid gas to its elemental form. Scheme S1 presents a simplified process flow diagram of OSTUM's upgrading process.



Scheme S1. Process flow diagram of OSTUM's upgrading process. The primary upgrading units (enclosed by blue rectangles) are a coking unit, a hydroconversion unit, or a combination of both.

Notes: Blue text indicates names of the most relevant process units in terms of energy use.

Flowcharts: OSTUM's Structure: Boundary, Energy Inputs, and GHG Emissions



Scheme S2. Flowchart showing OSTUM's boundary, energy inputs and GHG emissions.

Notes: Process units and utilities included within OSTUM's boundary (orange rectangle). Natural gas and electricity from the grid are produced outside the model's boundary but emissions associated with these are included in OSTUM (see below). Natural gas produced off-site is assumed to be used as fuel in all process units and also as feedstock in the steam methane reformer (SMR). If desired, fuel gas produced as a by-product by the upgrader can be used as a substitute for natural gas in all process heaters. Steam is produced on-site in utility boilers, in waste heat boilers, and in the cogeneration unit. It is used in almost all process units mainly for fractionation purposes. Electricity can be obtained from the grid and/or produced on-site through cogeneration. The hydrogen consumed by the hydroprocessing units is produced on-site via steam methane reforming, the most common practice in the upgrading industry. Coke is a by-product of the delayed coker and can be used as fuel in boilers. OSTUM accounts for the GHG emissions (thick light green arrows) generated by each process unit within its boundary (direct emissions),

and emissions generated off-site during the production of natural gas and electricity from the grid (indirect emissions).

Methods: Watson characterization factor, K_w

Crude oil and its fractions are complex mixtures containing large numbers of chemical species, mainly hydrocarbons. In order to correlate their physical properties with readily measurable parameters, correlations have been developed mainly in terms of standard density and the average normal boiling point.² The Watson characterization factor, K_w , (also known as the UOP characterization factor) is a correlation introduced by Watson and Nelson in 1933 to denote the paraffinicity of petroleum hydrocarbon fractions.³ The Watson characterization factor is defined as follows:

$$K_w = \frac{T_b^{1/3}}{s} \quad (1)$$

where T_b is the average normal boiling point in degrees Rankine ($^{\circ}\text{R}$) and s is the specific gravity at 60 degrees Fahrenheit ($^{\circ}\text{F}$). The value of K_w is an indication of the aromatic content of the hydrocarbon mixture, with lower values generally corresponding to greater aromatic content. Values of K_w typically fall within the range of 10 to 15: values around 10 correspond to highly aromatic materials, while values near to 15 correspond to highly paraffinic compounds.² In addition to characterizing the paraffinicity, K_w has been used to estimate other properties, like molecular weight and specific heat of petroleum fractions, percent hydrogen, kinematic viscosity, and critical temperature of petroleum-derived products.³

Methods: OSTUM's Crude Assay Inventory

OSTUM's feedstock database contains six diluted bitumen assays from the Athabasca region that are obtained from a public database⁴ and transformed according to a method proposed by Abella et al.⁵ to obtain all data needed. Each diluted bitumen and its crude fractions is characterized in terms of sulfur, nitrogen, and hydrogen content, API gravity, specific gravity, carbon residue, and its Watson characterization factor K_w . Table S1 presents the feedstocks included in OSTUM's database and their main properties.

Table S1. Diluted bitumen feedstocks included in OSTUM's assays database.

Diluted Bitumen	Production Overview	S (wt%)	N (mass ppm)	API Gravity	SG@ 60/60 °F	MCR (wt%)
Cold Lake (CL)	Asphaltic heavy crude blend of bitumen (11API/5.5%S) and condensate (65API/0.1%S). ⁶ Main producers are Imperial Oil Resources, Cenovus Energy, Canadian Natural Resources Limited and Shell Energy. ⁴	3.8	3,714.7	20.4	0.9	10.5
Western Canadian Select (WCS)	Heavy blended crude composed mostly of bitumen blended with sweet synthetic and condensate diluents and around 25 streams of both conventional and unconventional crudes. ⁷ Production managed by Canadian Natural Resources, Cenovus Energy, Suncor Energy, and Talisman Energy.	3.5	2,481.0	20.9	0.9	10.1
Christina Dilbit Blend (CDB)	Mixture of paraffins, naphthalenes, aromatic hydrocarbons and small amounts of sulfur and nitrogen compounds mixed with condensate. ⁸ Produced at the jointly owned Cenovus Energy Inc. and ConocoPhillips Christina Lake SAGD facility. ⁴	3.7	2,658.0	22.2	0.9	10.2
Borealis Heavy Blend (BHB)	Suncor Energy blend comprised of SAGD produced bitumen and hydrotreated naphtha/conventional diluent. ⁴	3.9	3,427.0	21.9	0.9	10.2
Access Western Blend (AWB)	Blend of bitumen and diluent produced by Devon Energy Canada and MEG Energy Corp. Production is generated by SAGD thermal methods. ⁴	3.8	3,741.1	22.1	0.9	10.4
Statoil Cheecham Blend (SCB)	Medium/heavy density, high sulfur blend of bitumen and diluent produced by Statoil using SAGD technology. ⁴	3.9	3,579.0	21.4	0.9	9.8

Abbreviations/Notes: S: sulfur content; N: nitrogen content; API: American Petroleum Institute gravity, a measure of how heavy or light a petroleum liquid is compared to water (if API gravity is greater than 10, it is lighter and floats on water; if less than 10, it is heavier and sinks); SG: specific gravity; MCR: Micro carbon residue.

The number of diluted bitumen assays available to the public is limited. The ones available in Crudemonitor,⁴ the only public database reporting current assays of different

Canadian crude oils, correspond to those of in-situ projects only. However, the majority of commercially upgraded bitumen comes from surface mining projects. Crudemonitor recently added the Kearl Lake (KDB) diluted bitumen assay, whose bitumen is “mined by shovel and truck and then undergoes onsite paraffinic froth treatment”⁴ before being sent to refineries able to process bitumen. Therefore, while this blend comes from a surface mining project, unfortunately it is not a representative mining-derived diluted bitumen feedstock due to the paraffinic solvent froth treatment it undergoes. Additionally, KDB is not upgraded in Alberta.

In our judgment, in-situ-derived diluted bitumen assays are reasonable to be used in OSTUM because the assay properties are expected to be very similar irrespective of the extraction process. To support this point, Table S2 compares key properties of the Cold Lake Blend employed as feedstock in OSTUM’s Comparison Scenario, (which was developed prior to KDB being available), the property ranges of the diluted bitumen assays in OSTUM’s database, and the properties of KDB.

Table S2. Comparison of key assay properties from OSTUM’s in-situ-derived Cold Lake Blend, other in-situ-derived diluted bitumens in OSTUM’s assay database, and the surface mined-derived diluted bitumen Kearl Lake Blend recently reported by Crudemonitor.⁴

Assay Properties	Cold Lake Blend from Comparison Scenario ⁴	Properties’ Ranges of Values in OSTUM’s Dilbit Assay Database ⁴	Kearl Lake Blend Assay ⁴
API	20	20-22	22
Sulfur Content, wt%	3.8	3.5-3.9	3.8
Nitrogen Content, wppm	3,715	2,481-3,741	3,328
Specific Gravity @ 60/60 °F	0.93	0.92-0.93	0.92
MCRT Carbon, wt%	10.5	9.8-10.5	8.4
Vacuum resid (525 °C+), wt%	44	40-44	43

Abbreviations: Dilbit: diluted bitumen.

Syncrude Canada⁹ has reported key properties of the diluted bitumen feedstock of its upgrading operations, but have not published a complete assay, which is required in order to incorporate it into OSTUM's crude assay inventory.

OSTUM's methods work appropriately with all diluted bitumens available in the model's crude assay inventory and, in general, with all Alberta crude oils that are chemically similar to diluted Athabasca bitumen (density: 922 – 928 kg/m³, gravity: 20 – 22 °API, sulfur content: 3.5 – 4.0 wt%). The simulation of other diluted bitumens assays in OSTUM is acceptable as long as they do not contain other conventional crudes. The model is not currently set up to deal with blends/dilutions of bitumen with SCO (synbits) or blends of various crudes.

Methods: Input Data Collection

OSTUM utilizes a set of input parameters that describe the process units' energy use per unit of feedstock (energy use factors), its operating conditions (e.g., temperature, pressure), and the properties of some feedstocks. Defaults and ranges of possible values for each input parameter are provided in OSTUM and obtained from public literature. Upgrading experts were consulted during the course of the research to ensure that the ranges of values for the input parameters were reasonable and our literature data sources were reliable. The following steps were taken in developing the defaults and ranges of values for the input parameters:

1. Collection of publicly available data from the refining literature (e.g.,^{10,11,12,13,14,15}), scientific journal papers (e.g.,^{16,17,18,9,19}), and life cycle assessment studies (e.g.,^{20,21,5}).
2. Development of a draft list of default values and ranges of possible values for the input parameters.
3. Consultation with upgrading experts, who provided feedback on the ranges of values for the input parameters and reliability of our literature data sources. The experts' role was mainly as a source of advice regarding data we obtained from literature. Their advice was also used to inform OSTUM's structure.
4. After minor refinements, the default values and ranges of input parameters were determined.

Methods: Hydrogen Consumption Calculation Methods Explored in OSTUM

Two different methods have been explored in developing OSTUM for the approximation of the hydrogen consumed by the hydroprocessing units (hydrocracker and hydrotreaters). As a first approach, hydrogen consumption was calculated following the “global hydrogen mass balance method” applied by Abella et al.⁵ and proposed by Castañeda et al.²² for the approximation of hydrogen use in refineries. In this method, the hydrogen requirement of each hydroprocessing unit is calculated by taking the difference in hydrogen content between the mass of the liquid feed and the mass of the hydrotreated liquid product and fuel gas. This method requires the determination of the hydrogen content in the liquid feed and product by analytical equipment or empirical correlations, and the determination of the total equivalent amounts of hydrogen contained in the gas streams entering and leaving the hydroprocessing units.²² In order to apply this method for the calculation of hydrogen consumption in the Petroleum Refinery Life Cycle Inventory Model (PRELIM),⁵ Abella et al. had to make several assumptions:

1. All crude feedstocks are processed to meet the same intermediate and final hydrotreater product hydrogen specifications, which means the hydrogen content of the hydrocracked/hydrotreated liquid is an assumption defined by the user of the model.
2. The hydroprocessing units are assumed to operate under the appropriate operating conditions (e.g., temperature, pressure) to produce a hydrocracked/hydrotreated product with the desired hydrogen content.

3. The mass yield, composition, and hydrogen content of the fuel gas produced by the hydroprocessing units are assumptions informed by expert input and might be changed by the user.
4. The extents of the hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions (i.e., percentage removal of sulfur and nitrogen in feed, the only hydroprocessing reactions accounted for in the method) are assumptions specified by the user to determine the amount of hydrogen added for this purpose.

Since the operation of hydroprocessing units in upgraders shares similarities with their refinery counterparts, the global hydrogen mass balance method and the assumptions previously listed were applied in the development of OSTUM's hydroprocessing units as a first approach to calculate make-up hydrogen consumption. Make-up hydrogen is the amount of hydrogen that has to be added to the hydroprocessing units to compensate for hydrogen chemically consumed in the hydrotreating reactions and the losses in the recycle gas system, and is the sum of chemical hydrogen consumption and hydrogen losses. However, an evaluation of OSTUM's global hydrogen mass balance method performed by upgrading scientists and industry experts revealed a number of concerns that needed to be addressed:

- The method's make-up hydrogen consumption results are highly sensitive to the values of hydrogen content that are assumed for the liquid hydrotreated product. Small variations in the assumed input values of hydrotreated products' hydrogen content may result in important differences in the hydrotreaters' hydrogen consumption estimates. This is of concern given that the hydrogen contents of feeds and hydrotreated products change significantly from one crude to another.

- Although the method uses the hydrotreaters' liquid product hydrogen content assumptions as proxies for the hydrogen chemically consumed in the hydroprocessing reactions, it does not allow the explicit calculation of chemical hydrogen consumption but only the approximation of make-up hydrogen by mass balance.
- The method assumes the conversion levels of sulfur and nitrogen impurities (i.e., the extents of HDS and HDN), rather than estimating them.
- The hydrotreaters' fuel gas yield is an assumption suggested by experts, and the rest of the product is hydrotreated liquid; therefore, the method does not allow the estimation of the yields of hydrotreated cuts (i.e., hydrotreated naphtha, LGO, and HGO) in each hydrotreater.
- The method doesn't allow for the investigation of the impact of operating conditions (e.g., temperature, pressure) on hydrogen consumption and product yields.

Using literature sources recommended by upgrading experts, a new method (hereinafter referred to as OSTUM's "hydrotreatment kinetic modeling method") was investigated and implemented for the estimation of chemical and make-up hydrogen consumption in OSTUM's hydroprocessing units. It consisted of the implementation of a number of literature kinetic models^{18,19,23} that calculate the extent of the hydrogenation reactions that consume most of the hydrogen in each type of hydroprocessing unit.

Naphtha Hydrotreater. When heavy hydrocarbons like oil sands bitumen are subjected to coking conditions, significant amounts of olefins and diolefins are formed in the

naphtha fraction in addition to the large amounts of sulfur, nitrogen, and aromatics. The presence of olefins and diolefins complicates the transportation and processing of coker naphtha (they polymerize at normal hydrotreating conditions, fouling the reactors and promoting the formation of coke); therefore, they must be hydrogenated before normal hydrotreating reactions (i.e., HDS, HDN, hydrodearomatization (HDA)) in order to stabilize the feed. A kinetic model proposed by Yui¹⁸ was implemented in the naphtha hydrotreater unit that approximates the extent of the hydrogenation of olefins, diolefins, and aromatics in the feed, and the levels of sulfur and nitrogen removal. The input parameters for the correlations are feed properties (i.e., feed's bromine number and diene number (indicators of olefins and diolefins contents, respectively), and the feed's aromatics, sulfur and nitrogen contents), the operating conditions (i.e., temperature, pressure, and liquid hourly space velocity (LHSV)), and kinetic parameters (activation energies and pre-exponential factors). The model assumes that all the reactions follow a modified first-order kinetics and that the Arrhenius equation applies to the rate constant.¹⁸ The hydrotreated product's properties can be estimated by the following equation:

$$C_p = \frac{C_f}{\exp\left(\exp\left(\ln(k_0) - \frac{E}{T+273.2} - \alpha \ln(\text{LHSV}) + \beta \ln(P)\right)\right)} \quad (2)$$

where:

- C_p : Product's bromine number, diene number, aromatics, sulfur, or nitrogen content (wt%)
- C_f : Feed's bromine number, diene number, aromatics, sulfur, or nitrogen content (wt%)
- k_0 : Pre-exponential factor ($\text{h}^\alpha \cdot \text{MPa}^{-\beta}$)

- E: Activation energy (cal/mol)
- R: Gas constant = 1.987 cal/mol*K
- T: Average catalyst bed temperature (°C)
- LHSV: Liquid hourly space velocity (h⁻¹)
- P: Reactor pressure (MPa)
- α, β : parameters determined by multiple linear regression using pilot plant data at various T, LHSV, and P

LGO and HGO Hydrotreaters. Distillates (LGO and HGO) obtained from oil sands bitumen are particularly high in aromatics, sulfur, and nitrogen. In fact, these bitumen-derived fractions can be much more aromatic than conventional distillates in the same boiling range.²⁴ Aromatics reduction is desirable to assist downstream refinery processing in reducing and achieving the total aromatics content of transportation fuels that meets the requirements of emission standards of diesel engines.²⁴ An effective means of reducing the aromatics concentration of middle distillates is by deep hydrogenation, but it tends to consume large amounts of hydrogen.²⁴ In the case of the LGO and HGO hydrotreaters, a kinetic model developed by Yui and Sanford¹⁹ was applied to predict the hydrogenation levels of aromatics and the removal of sulfur and nitrogen in the feed. The power law kinetic model assumes a first order reversible reaction. The fractional hydrogenation of aromatics is given by:

$$X_A = \frac{(k_f P^\beta - k_r M)}{(k_f P^\beta + k_r)} \left(1 - \exp \left(- \frac{(k_f P^\beta + k_r)}{LHSV^\alpha} \right) \right) \quad (3)$$

where:

- X_A : Fractional hydrogenation of aromatics
- k_f : Forward rate constant ($\text{h}^{-\alpha}\text{MPa}^{-\beta}$)
- k_r : Reverse rate constant ($\text{h}^{-\alpha}$)
- P : Reactor pressure (MPa)
- $LHSV$: Liquid hourly space velocity (h^{-1})
- M : Ratio of percentage of naphthenes and percentage of aromatics in the feed
- α : Power term for $LHSV$
- β : Power term for pressure

The kinetics of HDS reactions for bitumen-derived gas oils is assumed to obey 1.5th-order kinetics, while first-order kinetics are assumed for HDN reactions. The resulting equations for sulfur and nitrogen removal reactions are:

$$S_p = \frac{1}{\left[\left(\frac{k_s P^\beta}{2 LHSV^\alpha} \right) + \left(\frac{1}{S_f^2} \right) \right]^2} \quad (4)$$

where:

- S_p : Product's sulfur content (wt%)
- S_f : Feed's sulfur content (wt%)
- k_s : Reaction rate constant of HDS ($\text{h}^{-\alpha}\text{MPa}^{-\beta}$)
- P : Hydrogen partial pressure = reactor total pressure (MPa)
- $LHSV$: Liquid hourly space velocity (h^{-1})
- β : Power term for hydrogen partial pressure
- α : Power term for $LHSV$

$$N_p = N_{fexp} - \left(\frac{k_N P^\beta}{LHSV^\alpha} \right) \quad (5)$$

where:

- N_p : Product's nitrogen content (mass ppm)
- N_f : Feed's nitrogen content (mass ppm)
- k_N : Reaction rate constant of HDN ($\text{h}^{-\alpha} \text{MPa}^{-\beta}$)
- P : Hydrogen partial pressure = reactor total pressure (MPa)
- $LHSV$: Liquid hourly space velocity (h^{-1})
- β : Power term for hydrogen partial pressure
- α : Power term for LHSV

A method proposed by Edgar^{25,26} is subsequently used to approximate chemical hydrogen consumption by summing up the average contribution of each hydroprocessing reaction to obtain the total amount of hydrogen consumed:

$$HDS = \left[95 - 100 \frac{scf}{bbl} \right] \text{ per each 1 wt\% sulfur removed} \quad (6)$$

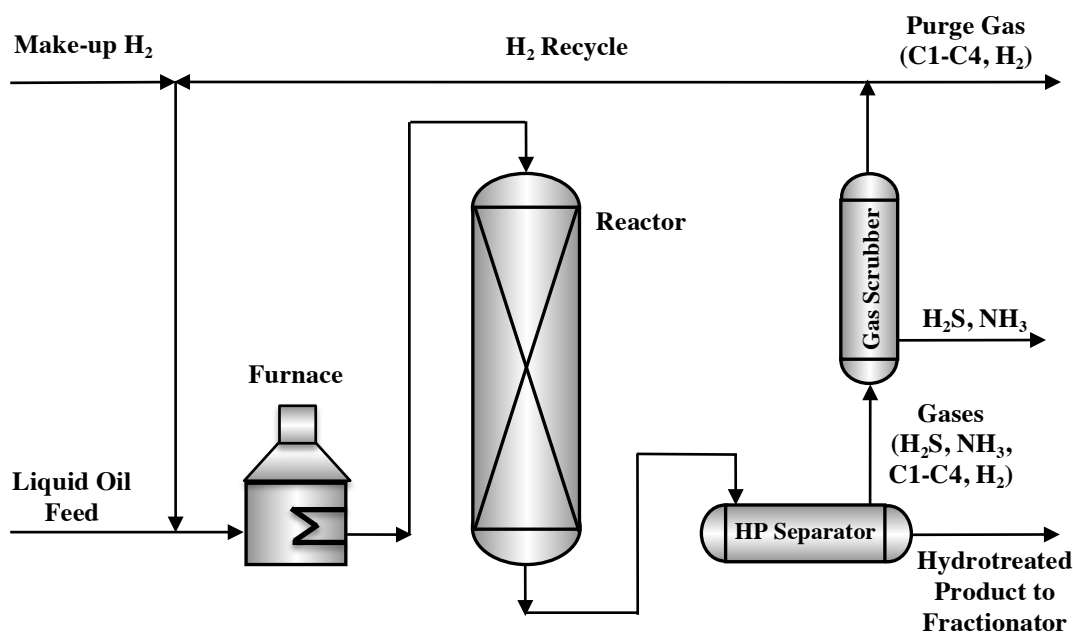
$$HDN = \left[300 - 350 \frac{scf}{bbl} \right] \text{ per each 1 wt\% of nitrogen removed} \quad (7)$$

$$HDA = \left[27 \frac{scf}{bbl} \right] \text{ per each 1 wt\% of aromatics saturated} \quad (8)$$

A global mass balance in the hydrotreater unit allows determination of the amount of make-up hydrogen consumed by the unit according to the expression:

$$\text{Make-up Hydrogen} = [\text{Chemical Hydrogen Consumption}] + [\text{Hydrogen Lost in Purge}] \quad (9)$$

The mass balances in the hydrotreaters also allow the determination of the mass flow rates of the rest of the input and output streams: liquid oil feed, liquid hydrotreated product, gas product, gases removed by the gas scrubber, purged gas, and amount of hydrogen recycled. An example of the streams involved in the hydrotreaters' mass balance is presented in Scheme S3.



Scheme S3. Flowchart showing the streams involved in OSTUM's hydrotreaters' mass balances.

The three hydrotreating processes included in OSTUM (naphtha, LGO, and HGO hydrotreating) share the same main elements and in general can be represented by the above schematic diagram. The liquid oil feed is mixed with hydrogen and brought to the reaction temperature using the feed furnace. The gas-liquid mixture is subjected to hydrotreating conditions in the main reactor (or a series of reactors). The reactor effluent is sent to a high-pressure separator (HP separator) where the liquid products are recovered from the gases and sent to a fractionator that separates various distillate products. The gases (mainly hydrogen sulfide (H_2S), ammonia (NH_3), light hydrocarbons (C1-C4)), and unreacted hydrogen (H_2)) are scrubbed with diethanolamine in order to remove the excess H_2S and NH_3 . Some of the sweet recycle gas is purged to prevent accumulation of H_2S and NH_3 and to control hydrogen partial pressure. The resulting high-purity hydrogen stream is recompressed and recycled to the reaction system.²⁷

Table S3 presents OSTUM's hydrogen consumption results obtained by the application of the global hydrogen mass balance method and by the application of OSTUM's hydrotreatment kinetic modeling method. In the left column of results, the global hydrogen mass balance method is applied in OSTUM's hydrotreaters using the Comparison Scenario liquid oil feeds and assuming typical hydrotreated product qualities found in the literature⁹ for a SCO blend upgraded from Athabasca bitumen (Syncrude Sweet Blend, SSB). The second column of results presents the hydrogen consumption results when the same method is applied in OSTUM's hydrotreaters assuming the Comparison Scenario's feed and product qualities. The third column of results displays the hydrogen consumption calculated by OSTUM's hydrotreatment kinetic modeling method when the Comparison Scenario set of conditions (temperature, pressure, space velocity, etc.) is applied. The sulfur and nitrogen contents of the hydrotreated products are calculated by the application of equations (2), (4), and (5), while the products' hydrogen contents are estimated by mass balances in the hydrotreaters reactors. The hydrogen consumption results obtained by OSTUM are compared to those obtained by the CanmetENERGY model (right hand column), a process simulation model developed by Natural Resources Canada.

Table S3. Hydrogen consumption results obtained by the application of the global hydrogen mass balance method⁵ and the hydrotreatment kinetic modeling^{18,19,23} in OSTUM, and by the CanmetENERGY model.^{16,17}

Process Units	Parameters / Hydrogen Consumption Results	Global Hydrogen Mass Balance Method Applied in OSTUM - CS Feeds' Quality, Products Quality from Literature ⁹	Global Hydrogen Mass Balance Method Applied in OSTUM - CS Feeds and Products' Quality	OSTUM's Hydrotreatment Kinetic Modeling Method - CS Feeds and Products' Quality	CanmetENERGY's Model Hydrogen Consumption Calculation Method - CS Feeds and Products' Quality
Naphtha HT	Feed H (wt%)	12.5	12.5	12.5	NA
	Feed S (wt%)	1.4	1.4	1.4	1.6
	Feed N (wppm)	412.5	412.5	412.5	231.2
	Product H (wt%)	13.8	13.6	13.6	NA
	Product S (wt%)	0.00055	0.01	0.01	0.02
	Product N (wppm)	9.0	17.8	17.8	9.9
	Chemical H₂ (scf/bbl)	NA	NA	556.3	584.3
	Make-up H₂ (scf/bbl)	720.0	561.7	582.5	NA
LGO HT	Feed H (wt%)	11.5	11.5	11.5	NA
	Feed S (wt%)	2.4	2.4	2.4	2.6
	Feed N (wppm)	822.8	822.8	822.8	778.7
	Product H (wt%)	12.7	12.8	12.8	NA
	Product S (wt%)	0.0118	0.02	0.02	0.11
	Product N (wppm)	58.0	88.2	88.2	204.2
	Chemical H₂ (scf/bbl)	NA	NA	738.7	805.0
	Make-up H₂ (scf/bbl)	692.9	739.9	751.4	NA
HGO HT	Feed H (wt%)	10.8	10.8	10.8	NA
	Feed S (wt%)	3.5	3.5	3.5	3.7
	Feed N (wppm)	2,468.0	2,468.0	2,468.0	2,097.0
	Product H (wt%)	12.2	12.4	12.4	NA
	Product S (wt%)	0.25	0.09	0.09	0.16
	Product N (wppm)	1,440.0	838.8	838.8	740.0
	Chemical H₂ (scf/bbl)	NA	NA	962.4	1,103.1
	Make-up H₂ (scf/bbl)	797.5	941.7	1,009.8	NA

HT: hydrotreater; LGO: light gas oil; HGO: heavy gas oil; CS: Comparison Scenario; H: hydrogen content; S: sulfur content; N: nitrogen content; H₂: hydrogen gas; NA: results not available for this study.

As previously discussed, the global hydrogen mass balance method does not explicitly calculate chemical hydrogen consumption in hydrotreaters; rather, it only calculates estimates of make-up hydrogen that account for the chemically consumed hydrogen plus other hydrogen losses. Also, the sensitivity of the global hydrogen mass balance method's hydrogen consumption results to the hydrogen content values that are assumed for liquid hydrotreated products is displayed in the analysis of the first two columns' results. A difference of 2% or less between the hydrogen content of the hydrotreated liquid products from the literature⁹ and from the Comparison Scenario results in a difference in hydrogen consumption estimates of up to 24%. This shows the variability in hydrogen consumption estimates that result from different assumptions of hydrogen

content of liquid products, a parameter for which ‘typical’ values are difficult to establish (hydrogen content changes significantly from one feed to another and therefore in their hydrotreated products). However, when the Comparison Scenario’s values of hydrogen content for hydrotreated products are assumed in the global hydrogen mass balance method, its hydrogen consumption results are very similar (within a 7% difference) to the results obtained by OSTUM’s hydrotreatment kinetic modeling method for the same Comparison Scenario. Therefore, the hydrogen mass balance method does a good job at reflecting the make-up hydrogen consumed by hydroprocessing units when appropriate values of hydrogen content are assumed for the feed and products. Given the difficulty in obtaining/establishing representative values for hydrogen content of hydrotreated products, a clear benefit of OSTUM’s hydrotreatment kinetic modeling method is its ability to estimate these values rather than assume them. Finally, percentage differences of 5%, 9%, and 14% are observed between the naphtha, LGO, and HGO hydrotreaters’ hydrogen consumption results (respectively) from OSTUM’s hydrotreatment kinetic modeling method and from CanmetENERGY’s model.

OSTUM’s hydrotreatment kinetic modeling method allows the estimation of parameters that were handled as model inputs for the application of the global hydrogen mass balance method (e.g., sulfur and nitrogen conversions, hydrogen content of hydrotreated products and of gas product) or parameters that were not explicitly calculated (e.g., the amount of hydrogen consumed by the main types of hydrotreating reactions, total chemical hydrogen consumption, aromatics conversion). The hydrogen consumption in hydrotreaters depends on feedstock properties, level of impurities removal, conversion level, and properties of the catalyst.²⁶ Hydroprocessing reactions occur on the catalyst’s

active sites; therefore, catalysts with the appropriate properties (pore structure, pore size distribution, etc.) are required to guarantee the access of reactant molecules to the active sites and the promotion of hydroprocessing reactions.²⁸ OSTUM's hydrotreatment kinetic modeling method takes into account all of these factors except the catalyst's properties (this is beyond OSTUM's current scope) and allows a further exploration of the parameters that affect hydrogen consumption. The method is particularly sensitive to variations in the average catalyst bed temperature of the hydrotreating reactors, since temperature is the most influential process variable (the extent and selectivity of hydrotreating and hydrocracking reactions are very sensitive to this operating condition because the reaction rate constants increase exponentially with temperature).²⁷ The conversion/hydrogenation of olefins, diolefins, sulfur, and nitrogen increases with temperature (and therefore the consumption of the hydrogen required by these reactions), although excessive temperatures must be avoided because of increased coke formation, loss of selectivity, higher catalyst deactivation, increased thermal cracking conditions, etc.^{24,29,27} The conversion of aromatics is also highly dependent on temperature and increases with increasing reactor temperature at first, but after reaching the equilibrium limit decreases as the temperature is further increased (increased hydrogenation levels might be achieved with decreased space velocity or increased pressure).¹⁹ Other operating conditions like pressure and space velocity also impact the levels of conversion (increasing pressure increases sulfur and nitrogen removal, hydrogen saturation and hydrogen consumption ultimately; increasing space velocity reduces conversion and hydrogen consumption),²⁹ but they are usually fixed in hydrotreating operations. The effects of temperature in the conversion and hydrogen consumption of hydrotreating reactions can be reproduced by OSTUM's hydrotreatment kinetic modeling method.

Figure S1 presents the chemical hydrogen consumption calculated by OSTUM for each hydrotreating unit when the average catalyst bed temperature of the reactors was varied within $\pm 40^{\circ}\text{C}$ from the Comparison Scenario temperatures. Sulfur conversion (HDS reactions) is presented as indicator of the change in conversion levels obtained when the operating temperature is varied.

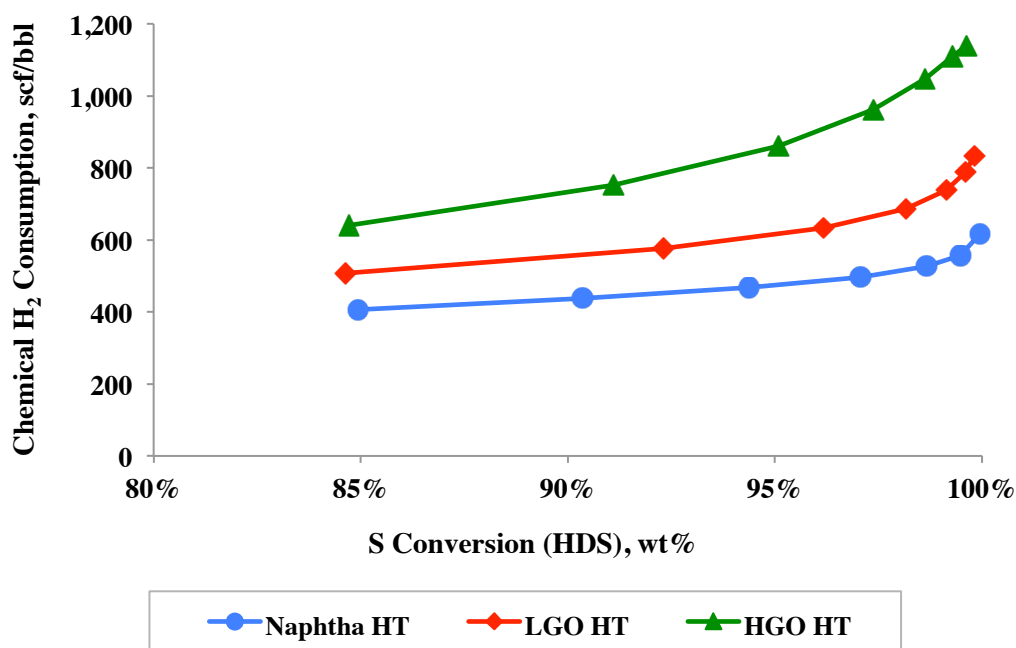


Figure S1. Chemical hydrogen consumption and sulfur conversion (HDS) calculated by OSTUM for a range of temperatures ($\pm 40^{\circ}\text{C}$ from Comparison Scenario temperatures) for the three upgrader's hydrotreaters.

Notes: The Comparison Scenario temperatures for each hydrotreater are: naphtha hydrotreater: 285°C ; LGO hydrotreater: 340°C ; HGO hydrotreater: 370°C .

Abbreviations: H_2 : hydrogen gas; S: sulfur; HDS: hydrodesulfurization; HT: hydrotreater.

OSTUM's hydrotreating kinetic modeling method responds well to temperature variations and is capable of generating reasonable ranges of hydrogen consumption and conversion in accordance with typical operating conditions of temperature, pressure, and space velocity. For a range of 85-100% sulfur conversion, OSTUM calculates a range in chemical hydrogen consumption of 406-618 scf/bbl (make-up hydrogen: 438-642 scf/bbl)

for the naphtha hydrotreater, 507-834 scf/bbl (make-up hydrogen: 520-844 scf/bbl) for the LGO hydrotreater, and 641-1,139 scf/bbl (make-up hydrogen: 689-1,187 scf/bbl) for the HGO hydrotreater. These ranges are in accordance with the levels of hydrogen consumption reported in the literature^{13,27} for the hydrotreating of heavy oil/bitumen-derived fractions. Literature usually provides general ranges of hydrogen consumption for the hydrotreating of heavy oil (400-1,000 scf/bbl),¹³ and residue (592-1036 scf/bbl,²⁷ 600-1,200 scf/bbl),¹³ which is the fraction with a boiling point over 524°C that constitutes around 52 wt% of bitumen.

The accurate estimation of hydrogen consumption in actual operations is a very complex task. Calculating the exact hydrogen consumption involves the extremely difficult (if not impossible) task of counting the moles of hydrogen added to each of the millions of hydrocarbon molecules reacted. The use of kinetic models is an alternative approach to *approximate* hydrogen consumption. By first calculating key properties (e.g., aromatics, sulfur, and nitrogen contents) of the hydroprocessed products, hydrogen consumption can then be approximated as a function of feedstock and product properties. OSTUM's hydrotreating kinetic modeling method works for a range of hydroprocessing scenarios with similar operating conditions, reactor types, catalysts, and feedstock compositions to the ones originally employed to develop the literature kinetic models.^{18,19,23} For hydrotreating scenarios with significant variations in these parameters, new experimental data would be needed to obtain good estimations. However, the relatively small variations in the properties of Athabasca bitumen and in the operating conditions of bitumen hydroprocessing units allow the use of OSTUM's hydrotreating kinetic modeling method.

Methods: Calculation of Product Yields in OSTUM

OSTUM calculates the product yields of the diluent recovery unit and the vacuum distillation unit using distillation curve data obtained by high-temperature simulated distillation (HTSD) of commercial diluted bitumen blends. The distillation results are published by Crude Quality Inc. in the public database Crudemonitor⁴, which monitors and reports crude quality data for a variety of Canadian crudes. The method to calculate product yields from crude distillation curve data is reported in detail in Supporting Information of Abella et al.⁵

The product yields from the delayed coker are calculated using a set of linear correlations developed by Volk et al.³⁰ in a micro-coker model that correlates experimental yields with four different characteristics of the delayed coker feed (API gravity, micro carbon residue (MCR), asphaltenes (C5+), and asphaltenes (C7+)). The authors found that MCR gives the best correlation for most of the delayed coker products. The general product yield correlations using MCR as feed characteristic are:³⁰

$$\text{Liquid Products} = -1.1139MCR + 0.0419T - 0.2897P + 1103.08LSV + 41.59 \quad (10)$$

$$\text{Gas} = 0.1729MCR + 0.0191T + 0.13646P - 786.319LSV - 6.762 \quad (11)$$

$$\text{Naphtha} = -0.3086MCR + 0.0137T + 0.1571P - 819.63LSV + 16.461 \quad (12)$$

$$\text{LCGO} = -0.3339MCR - 0.02635T - 0.0392P + 70.957LSV + 50.452 \quad (13)$$

$$\text{HCGO} = -0.4714MCR + 0.0546T - 0.4076P + 1851.76LSV - 25.315 \quad (14)$$

$$\text{Coke} = 0.9407MCR - 0.0609T + 0.1529P - 319.759LSV + 65.075 \quad (15)$$

where:

- *MCR*: Micro carbon residue

- T : Temperature (°F)
- P : Pressure (psig)
- LSV : Liquid space velocity (min^{-1})

Scale-up issues are observed when using the previous micro-coker model correlations to predict the yields from industrial cokers.³⁰ First, the liquid yields obtained are lower than those observed in refineries' delayed cokers. Second, the correlations include a term to account for the effects of the residence time in product yields that does not have the same meaning in commercial units. Liquid space velocity in the micro-coker model is defined based on the reactor volume, which makes sense for this reactor but does not for a commercial coker, where the coking reactions start before the material enters the drum.³⁰ Therefore, the authors adjusted the correlations to better simulate the performance of an industrial delayed coker and predict its product yields:³⁰

$$\text{Adjusted Coke} = \text{Coke} \times 0.91 \quad (16)$$

$$\text{Adjusted Gas} = \text{Gas} \times 0.82 \quad (17)$$

$$\text{Adjusted Liquid Products} = 100 - (\text{Adjusted Coke} + \text{Adjusted Gas}) \quad (18)$$

$$\text{Adjusted Naphtha} = \text{Naphtha} \times \frac{\text{Adjusted Liquid Products}}{\text{Liquid Products}} \times 0.75 \quad (19)$$

$$\text{Adjusted LCGO} = \text{LCGO} \times \frac{\text{Adjusted Liquid Products}}{\text{Liquid Products}} \times 0.90 \quad (20)$$

$$\text{Adjusted HCGO} = \text{Adjusted Liquid Products} - (\text{Adjusted Naphtha} + \text{Adjusted LCGO}) \quad (21)$$

The ranges of validity for these empirical correlations are: temperature from 900 to 950 °F, pressure from 6 to 40 psig, and micro carbon residues from 16 to 29 wt%. The correlations are not expected to give good predictions outside of these ranges. In addition,

they do not account for the prediction of specific gaseous species (H_2S , NH_3 , C1-C4) nor unconverted residue (vacuum residue).

Although hydrotreaters are not conversion units, hydrocracking reactions in some of these units are somewhat important.³¹ Mild hydrocracking reactions in LGO and HGO hydrotreaters produce additional amounts of naphtha and LGO that have an effect on SCO quality and composition (degree of conversion: 5 – 15 wt%).³¹ Conversion levels in naphtha hydrotreaters are minimal (0 – 5 wt%).³¹ Therefore, while hydrocracking reactions in the naphtha hydrotreater are assumed to be negligible, a kinetic model developed by Yui and Sanford²³ is used to estimate the product yields of naphtha and LGO fractions in the LGO and HGO hydrotreaters. The model is developed using Athabasca bitumen-derived coker and hydrocracker HGOs as feed to a pilot-scale trickle-bed reactor. The degree of conversion of the HGOs into LGO and naphtha is analyzed with modified first-order kinetic equations. The hydrocracking reactions are described reasonably well either by a first-order parallel conversion scheme in which HGO converts simultaneously into LGO and naphtha, or by a consecutive conversion scheme where HGO first converts into LGO and then LGO converts into naphtha. Assuming a consecutive conversion scheme, the fractions of HGO, LGO, and naphtha in the hydrotreated liquid product are given by:

$$C_{\text{HGO}} = C_{\text{HGO}_0} \exp\left(-\frac{k_1 P^\beta}{\text{LHSV}^\alpha}\right) \quad (22)$$

$$C_{\text{LGO}} = C_{\text{LGO}_0} \exp\left(-\frac{k_3 P^\beta}{\text{LHSV}^\alpha}\right) + \frac{k_1}{(k_3 - k_1)} C_{\text{HGO}_0} \left[\exp\left(-\frac{k_1 P^\beta}{\text{LHSV}^\alpha}\right) - \exp\left(-\frac{k_3 P^\beta}{\text{LHSV}^\alpha}\right) \right] \quad (23)$$

$$C_{\text{N}} = C_{\text{HGO}_0} + C_{\text{LGO}_0} + C_{\text{N}_0} - C_{\text{HGO}} - C_{\text{LGO}} \quad (24)$$

where:

- C_{HGO} : Fraction of HGO in product (% of HGO in product)

- C_{HGO_0} : Fraction of HGO in feed (% of HGO in feed)
- k_1, k_3 = reaction rate constants for step 1 (HGO to LGO), and step 3 (LGO to naphtha), respectively
- P : Hydrogen partial pressure = reactor total pressure (MPa)
- β : Power term for hydrogen partial pressure
- LHSV: Liquid hourly space velocity (h^{-1})
- α : Power term for LHSV
- C_{LGO} : Fraction of LGO in product (% of LGO in product)
- C_{LGO_0} : Fraction of LGO in feed (% of LGO in feed)
- C_N : Fraction of naphtha in product (% of naphtha in product)
- C_{N_0} : Fraction of naphtha in feed (% of naphtha in feed)

Finally, the yield of total liquid products is given by the equation:

$$Y = Y_o \left(\frac{T}{400} \right)^a \left(\frac{P}{10} \right)^b LHSV^c \quad (25)$$

where:

- Y : Total volume yield of hydrotreated liquid products (m^3/m^3 feed)
- Y_o : Constant (m^3/m^3 feed)
- T : Temperature ($^{\circ}C$)
- P : Hydrogen partial pressure = reactor total pressure (MPa)
- LHSV: Liquid hourly space velocity (h^{-1})
- a, b, c : power terms for temperature, hydrogen partial pressure, and LHSV, respectively

The densities of hydrotreated products are used with the previous equations to obtain the mass yield of hydrotreated products.

Methods: OSTUM's Emissions Factors

The life cycle-based emissions factors used in OSTUM to calculate direct and indirect upgrading GHG emissions are presented in Table S4.

Table S4. Default direct and indirect emissions factors in OSTUM.

Energy Input	Type of Emissions	Emissions Factor	Unit	Reference
Natural gas	Direct emissions from combustion of natural gas	56.6	g CO ₂ e/MJ natural gas	³²
Natural gas	Direct emissions from reaction of natural gas in steam methane reforming	56.3	g CO ₂ e/MJ natural gas	³²
Natural gas	Indirect upstream emissions from natural gas production process	9.9	g CO ₂ e/MJ natural gas	³²
Fuel gas	Direct emissions from combustion of fuel gas	56.6	g CO ₂ e/MJ fuel gas	³²
Electricity from coal-fired generation system	Indirect upstream emissions from electricity generation process	287.2	g CO ₂ /MJ electricity	³³
Electricity from natural gas-fired generation system	Indirect upstream emissions from electricity generation process	138.9	g CO ₂ /MJ electricity	³³
Electricity from the Alberta electricity generation mix in 2013	Indirect upstream emissions from electricity generation process	197.8	g CO ₂ /MJ electricity	³³

The emissions factors utilized in OSTUM's Comparison Scenario are those associated with the use of natural gas as fuel, natural gas as feedstock to the SMR, and with electricity generated by an off-site natural gas-fired system. Sensitivity analyses were conducted with the purpose of investigating the impact of alternative emissions factors and natural gas heating values on OSTUM's Comparison Scenario upgrading emissions. The alternative emissions factors and heating values explored are those proposed by GHGenius v. 4.03³⁴ and the latest version of the GREET model (GREET 1 2015).³⁵ Table S5 displays the results of these sensitivity analyses.

Table S5. Sensitivity analyses on OSTUM's Comparison Scenario GHG emissions when alternative heating values for natural gas, and alternative natural gas and electricity emission factors are assumed.

OSTUM's Comparison Scenario GHG Emissions Using Different Sources of Natural Gas Heating Values and Emissions Factors				
	Direct Emissions	Indirect Emissions	Total Emissions	% Difference in Emissions w.r.t. Comparison Scenario
Natural Gas Heating Values				
OSTUM's Comparison Scenario: HHV = 52.59 MJ/kg (LHV = 47.44 MJ/kg) ³⁶	261	67	328	0%
GHGenius v. 4.03's HHV = 52.46 MJ/kg (LHV = 46.53 MJ/kg) ³⁴	260	67	327	0%
REET 1 2015's HHV = 52.23 MJ/kg (LHV = 47.14 MJ/kg) ^{32, 35}	259	67	326	1%
Emissions Factors				
OSTUM's Comparison Scenario				
Direct EF NG-Fuel = 56.63 gCO ₂ e/MJ				
Direct EF NG-Feedstock-SMR = 56.31 gCO ₂ e/MJ natural gas consumed	261	67	328	0%
Indirect EF NG = 9.88 gCO ₂ e/MJ				
EF Electricity from NG-Fired System = 138.89 gCO ₂ e/MJ				
GHGenius v. 4.03³⁴				
Direct EF NG-Fuel = 50.58 gCO ₂ e/MJ				
Direct EF NG-Feedstock-SMR = 50.48 gCO ₂ e/MJ natural gas consumed	233	65	298	10%
Indirect EF NG = 9.61 gCO ₂ e/MJ				
EF Electricity from NG/turbine = 132.70 gCO ₂ e/MJ				
REET 1 2015³⁵				
Direct EF NG-Fuel = 56.52 gCO ₂ e/MJ				
Direct EF NG-Feedstock-SMR = 8.77 gCO ₂ e/MJ H ₂ produced*	260	61	321	2%
Indirect EF NG = 8.73 gCO ₂ e/MJ				
EF Electricity from NG-Fired System = 131.43 gCO ₂ e/MJ				

* Could not be applied in OSTUM because of difference in functional units and lack of a factor to convert them

Abbreviations: HHV: higher heating value of a fuel; LHV: lower heating value of a fuel; EF: emission factor; NG: natural gas; SMR: steam methane reformer; w.r.t.: with respect to.

In general, OSTUM's Comparison Scenario upgrading emissions don't change when the higher heating values (HHVs) of natural gas proposed by GHGenius and REET replace the default values in the model. There is, however, a 10% deviation in upgrading emissions using GHGenius' emission factors for natural gas and electricity, and a 2% deviation using REET's. However, REET's emissions factor associated with the use of natural gas as feedstock in the SMR could not be applied in OSTUM. This emissions

factor is provided by GREET in a different functional unit (MJ of hydrogen produced) than the one used in OSTUM (MJ of natural gas consumed) and an appropriate conversion factor could not be located.

It is important to highlight that many of the oil sands operators purchase or produce natural gas from the oil sands region. However, not all projects consume natural gas from the same place – some also comes from fracking operations in Alberta and British Columbia. Therefore, there are no specific natural gas heating values and emissions factors that can be utilized as defaults. Having available ranges of relevant HHVs, LHVs, and emission factors is OSTUM's approach, and the model's database will continue to be improved in future versions.

OSTUM allows a user to specify the use of HHVs or LHVs of the fuels used in the upgrading process. The LHV/HHV switch is also sensitive to electricity consumption.

Methods: Input Parameters and GHG Emissions Calculations in Process Units

Table S6. Parameters used to estimate product yields and energy use in OSTUM's process units, and their associated direct and indirect emissions calculations.

Process Unit	Feed	Process Objective	Products	Parameters Defining Yields	Parameters Defining Energy Use	Direct Emissions Calculation	Indirect Emissions Calculation
Diluent Recovery	Dilbit	Separate and recover the diluent from the bitumen. The diluent is sent back to the extraction plant for reuse.	<ul style="list-style-type: none"> Diluent ATB 	<ul style="list-style-type: none"> Distillation curve of dilbit Cut Ts 	NG, electricity and steam use / volume of feed	DE = (NG volume * NG combustion EF) + (FG volume * FG combustion EF)	IE = (NG volume * NG upstream EF) + (amount of electricity * electricity generation technology/ electrical grid EF)
Vacuum Distillation	ATB	Separate and remove the naphtha, LGO and HGO from the bottoms and direct these streams to the HTs	<ul style="list-style-type: none"> Naphtha LGO HGO VTB 	<ul style="list-style-type: none"> Distillation curve of dilbit Cut Ts 	NG, electricity and steam use / volume of feed	DE = (NG volume * NG combustion EF) + (FG volume * FG combustion EF)	IE = (NG volume * NG upstream EF) + (amount of electricity * electricity generation technology/ electrical grid EF)
DC	VTB	Crack the long chain hydrocarbon molecules in VTB into short chain ones, increasing their H/C ratio, rejecting carbon as coke	<ul style="list-style-type: none"> Coker sour gas Coker naphtha LCGO HCGO Coke 	<ul style="list-style-type: none"> LHSV Reaction T Reaction P MCR carbon of feed 	NG, electricity and steam use / volume of feed	DE = (NG volume * NG combustion EF) + (FG volume * FG combustion EF)	IE = (NG volume * NG upstream EF) + (amount of electricity * electricity generation technology/ electrical grid EF)
Naphtha, LGO, and HGO HTs	<ul style="list-style-type: none"> Naphtha HT: naphtha and coker naphtha LGO HT: LGO and LCGO HGO HT: HGO and HCGO 	Remove and reduce S, N, metal compounds, aromatics, and other impurities	<ul style="list-style-type: none"> Hydro-treated naphtha Hydro-treated LGO Hydro-treated HGO Sour gas 	<ul style="list-style-type: none"> Feed's S and N content T and P of reaction LHSV Kinetic parameters 	<ul style="list-style-type: none"> NG, electricity and steam use / volume of feed Feed's Br and diene numbers, S, N, Ar contents Reaction T, P LHSV Kinetic parameters 	DE = (NG volume * NG combustion EF) + (FG volume * FG combustion EF)	IE = (NG volume * NG upstream EF) + (amount of electricity * electricity generation technology/ electrical grid EF)
Amine Treatment and Amine Regeneration	Sour gases from DC and HTs	Remove H ₂ S and CO ₂ from sour gases	FG	H ₂ S yield from DC and HTs	Electricity and steam consumption / volume of feed	None	IE = amount of electricity * electricity generation technology/ electrical grid EF
Claus Sulfur Recovery / Claus Tail Gas Treatment	H ₂ S removed from sour gases	Desulfurize acid gas, recover elemental S from H ₂ S	<ul style="list-style-type: none"> S Tail gases 	Typical recovered S yield	NG and electricity consumption / volume of feed	DE = (NG volume * NG combustion EF) + (FG volume * FG combustion EF)	IE = (NG volume * NG upstream EF) + (amount of electricity * electricity generation technology/ electrical grid EF)

Table S6. Continued.

Process Unit	Feed	Process Objective	Products	Parameters Defining Yields	Parameters Defining Energy Use	Direct Emissions Calculation	Indirect Emissions Calculation
SMR	NG	Produce hydrogen required by the HTs	Hydrogen	Total hydrogen demand from HTs	NG, electricity and steam use / volume of feed	DE = (NG volume * NG combustion EF) + (NG volume * chemical reaction of NG EF) + (FG volume * FG combustion EF)	IE = (NG volume * NG upstream EF) + (amount of electricity * generation technology/ electrical grid EF)
Boilers	Feed water	Create steam by applying heat energy to water	Steam	Total steam demand from processing units	Fuel, electricity and steam use / volume of feed	DE = (NG volume * NG combustion EF) + (FG volume * FG combustion EF) + (carbon content of coke * ratio of molecular weight of CO ₂ (44 g/mol) to molecular weight of carbon (12 g/mol))	IE = (NG volume * NG upstream EF) + (amount of electricity * generation technology/ electrical grid EF)
Cogen	NG	Simultaneous generation of electricity and heat	<ul style="list-style-type: none"> • Electricity • Steam 	Total electricity produced	<ul style="list-style-type: none"> • Efficiency of gas turbine • Efficiency of HRSG • Electricity demanded 	DE = NG volume * NG combustion EF	IE = NG volume * NG upstream EF

Abbreviations: Dilbit: diluted bitumen; ATB: atmospheric topped bitumen; VTB: vacuum topped bitumen; NG: natural gas; FG: fuel gas; DE: direct emissions; IE: indirect emissions; EF: emissions factor; LGO: light gas oil; HGO: heavy gas oil; DC: delayed coker; HT: hydrotreater; SMR: steam methane reformer; Cogen: cogeneration unit; LCGO: light coker gas oil; HCGO: heavy coker gas oil; LHSV: liquid hourly space velocity; MCR: micro carbon residue; T: temperature; P: pressure; S: sulfur; N: nitrogen; Br: bromine; Ar: Aromatic; H₂S: hydrogen sulphide; CO₂: carbon dioxide; HRSG: heat recovery steam generator

Linear Relationship Assumption Between Process Units' Energy Requirements and

Feed. The assumption that the upgrader's process energy requirements are linearly related to the process units' volume and/or mass feed flows is supported by energy use in refineries and upgraders being driven by the process units that process large volumes of feedstock.³⁷ For example, the DRU and the SMR represent ~63% of the Comparison Scenario's energy use. The reason is that any barrel of oil entering the upgrader runs through the DRU, and SMR is the only source of hydrogen to meet the hydrogen demand of the upgrader's hydrotreating units. On the other hand, when the throughput of a

process unit is increased, the efficiency of the unit might increase as well, due to the integration of the heat and steam systems within an upgrader for energy saving purposes. However, if the increase in throughput is not significant (e.g., double or triple of the original), the assumption linearly correlating process units' energy requirements with feed flow rates is expected to still be reasonable.

Methods: Natural Resources Canada's CanmetENERGY Model

A study performed by Natural Resources Canada's CanmetENERGY evaluating commercial bitumen upgrading technologies through process modeling and simulation resulted in the publication of the CanmetENERGY model in 2013.^{16,17} The model is developed in Aspen HYSYS and simulates both delayed coking and hydroconversion technologies. It calculates the product yields, chemical hydrogen consumption, relevant oil properties (e.g., API gravity, sulfur, nitrogen, aromatics contents), energy use, and CO₂ emissions at each upgrading step under different operating conditions. The upgrading stages included are feedstock separation, primary upgrading, and secondary upgrading. The process units modeled are DRU, vacuum distillation unit, delayed coker, ebullated-bed hydrocracker, naphtha hydrotreater, LGO hydrotreater, and HGO hydrotreater. The hydrogen demanded by the hydroprocessing units is produced through steam methane reforming.¹⁷ Although the energy use of the SMR is not explicitly modeled, its emissions are taken into account using an emissions factor obtained from the literature^{20,17}. Most of the process units are modeled using HYSYS's built-in modules; however, to predict the performance of process units not included in HYSYS (delayed coker, ebullated-bed hydrocracker, and naphtha hydrotreater), literature kinetic models are implemented in the simulator and adjusted with proprietary pilot plant data.¹⁶ The simulation's main input parameters include: crude assay data (true boiling point distillation curve data, density, sulfur, nitrogen, aromatics, metals, and asphaltenes distributions), operating conditions of each process unit (e.g., temperature, pressure, space velocity), kinetic rate parameters for the different reactors, and process specifications in some process units (e.g., distillation columns' cut points of crude fractions, reflux rate, stripping steam rate). The energy inputs quantified by the model are

natural gas as fuel for fired heaters, steam as stripping agent, electricity, and hydrogen for the hydroprocessing units.¹⁷ Different calculation approaches are used to calculate these commodity inputs: HYSYS built-in process modules and literature kinetic models tuned with proprietary pilot plant data, mass and energy balances, process units' design factors, turbine calculations, and the methodology proposed by Ordorica-Garcia et al.³⁸ to estimate energy use in upgraders. It should be noted that the kinetic models implemented in the CanmetENERGY model have the fundamental limitation of being feedstock dependant and therefore, are valid only for Alberta's oil sands heavy crudes. To extend their application to oils with different composition and geographic origin, the model parameters must be refitted using pertinent experimental data. The CanmetENERGY model assumes natural gas is the only fuel utilized for the production of heat, steam, electricity and hydrogen.¹⁷ The use of byproducts fuel gas, steam, and/or coke is not accounted for in the model. Finally, the estimation of CO₂ emissions is based on equations published in³⁸ and representative literature emission factors.¹⁷ The model is designed to estimate mainly direct CO₂ emissions; the only indirect emissions accounted for are from electricity production. More detailed information about the CanmetENERGY model can be found in^{16,17}.

Methods: OSTUM and CanmetENERGY Models Key Attributes

Table S7. Comparison of OSTUM and CanmetENERGY model's key attributes.

	OSTUM	CanmetENERGY Model
Authors	Pacheco, D. M., Bergerson, J. A., MacLean, H. L.	Alvarez-Majmutov, A., Chen, J.
Publication Year	2016 (present paper)	2013
Upgrading Technologies	Delayed coking-based, ebullated-bed hydroconversion-based, combined hydroconversion and fluid coking-based upgrading	Delayed coking, ebullated-bed hydrocracking
Process Units	Diluent recovery unit, vacuum distillation unit, delayed coker/ebullated-bed hydrocracker, naphtha hydrotreater, LGO hydrotreater, HGO hydrotreater, amine treatment and amine regeneration units, sulfur recovery unit, steam methane reformer, boilers, and cogeneration unit	Diluent recovery unit, vacuum distillation unit, delayed coker/ebullated-bed hydrocracker, product fractionator, naphtha hydrotreater, LGO hydrotreater, HGO hydrotreater, steam methane reformer, and boilers
Energy Inputs	Natural gas, fuel gas, coke, steam, hydrogen, and electricity	Natural gas, steam, hydrogen, and electricity
Type of Input Parameters	Diluted bitumen blend, upgrading and electricity generation technologies, byproducts used as energy inputs, emissions allocation method, energy consumption factors for each process unit, reaction conditions for primary and secondary upgrading process units, and some intermediate products quality indicators	Diluted bitumen blend, upgrading technology, operating/reaction conditions for each process unit, and emission factors
Data Sources	Public literature	Public literature, proprietary pilot-plant data, engineering judgment
Software and Calculation Methods	Excel * <i>Energy use</i> : calculations using crude distillation curve data, energy consumption factors for each process unit, mass and energy balances, product yield correlations, literature kinetic models * <i>GHG emissions</i> : calculations using energy consumption results and emissions factors	Aspen HYSYS * <i>Energy use</i> : Thermodynamic modeling with the Peng-Robinson equation of state, HYSYS's Petroleum Refining tool, Petroleum Shift Reactor tool, Assay Manipulator tool, literature kinetic models, mass and energy balances * <i>CO₂ emissions</i> : calculations using energy consumption results and emissions factors
Type of Results	Product yields and selected product quality properties, total energy use, energy use from each type of energy input and process unit, GHG emissions in different functional units (g CO ₂ e/MJ product, g CO ₂ e/bbl crude feedstock, g CO ₂ e/MJ SCO, kg CO ₂ e/m ³ SCO)	Product yields and product properties, total energy use, energy use from each type of energy input and process unit, impact of operating conditions in primary upgrading reactor performance, GHG emissions in kg CO ₂ /m ³ SCO, kg CO ₂ /bbl SCO

Abbreviations: LGO: light gas oil; HGO: heavy gas oil

Methods: Justification of the Comparison Scenario

The Comparison Scenario has been specified to represent a realistic upgrading operation and illustrate the capabilities of OSTUM. The Comparison Scenario is not meant to reflect a specific commercial upgrading operation as there is considerable variability in these operations and the detailed data required to replicate an operation (the exact diluted bitumen feedstock, process configuration, operating conditions, energy inputs, etc.) are not publicly available. Rather, the purpose of its formulation is to facilitate the comparison and evaluation of OSTUM with relevant literature. The Comparison Scenario assumes a delayed coking-based upgrading operation with a capacity of 400,000 barrels per day of diluted bitumen feedstock. The feedstock is Cold Lake Blend, since it is the most well-known and representative Alberta bitumen for which assay data is publicly-available.⁴ Natural gas is specified as the process fuel for heat, steam and hydrogen production. The operation produces SCO (blend of naphtha, LGO, and HGO), fuel gas and coke. SCO is considered the main product and the others by-products. The by-products are assumed to not be used for process energy in the Comparison Scenario. Instead, fuel gas is assumed to be flared (flaring emissions are included in results) and coke is assumed to be stockpiled. Current low prices of natural gas make it unattractive to sell fuel gas and therefore it is considered a by-product rather than co-product. Only one of the two commercial delayed coking-based upgrading projects currently operating (Suncor's U1/U2 upgrading plant) burns a small fraction of its coke to produce steam, but this amount changes significantly from month to month,³⁹ as shown by Figure S2. Therefore, stockpiling the coke is currently the most common practice in the industry and the assumption of the Comparison Scenario.

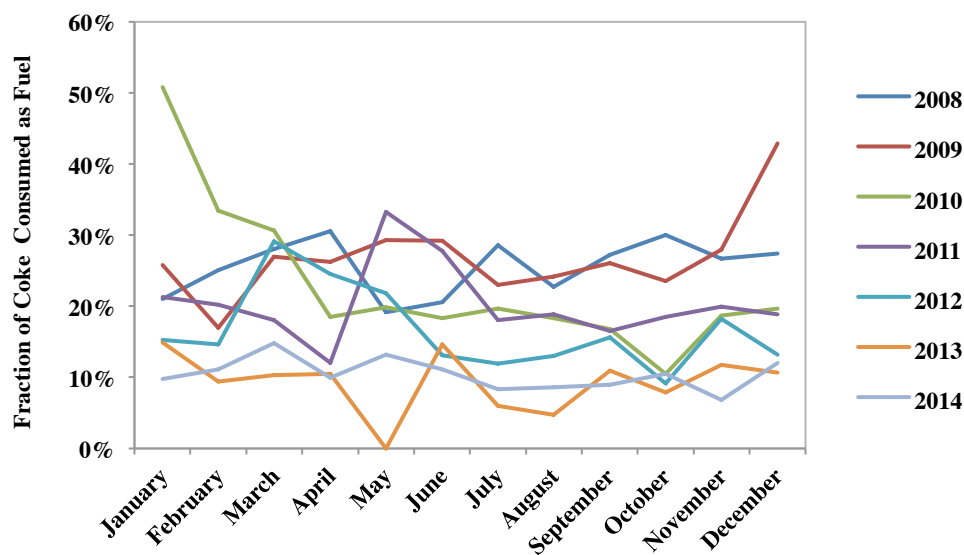


Figure S2. Monthly fraction of Suncor’s by-product coke burnt as fuel in boilers to produce steam, for 2008 – 2014. Data source: AER’s ST-39 report.³⁹

Since SCO is considered the only product in the Comparison Scenario, energy use and GHG emissions (direct and indirect) are allocated only to it. Other products (e.g., fuel gas and coke) are assumed to be by-products and are not allocated emissions. Therefore, no allocation method is used in this scenario.

Electricity is assumed to be obtained from an off-site natural gas-fired generation plant (i.e., natural gas combined cycle power plant). This assumption is reasonable considering Alberta’s electricity grid mix. Although 55% of the electricity generated in Alberta in 2014 came from coal, as of August 2015 about 44% of Alberta’s installed electricity generation capacity is from natural gas, while 38% is from coal.⁴⁰ In addition, around 62% of the new installed capacity being added to Alberta through new generation projects comes from natural gas-fueled power plants, around 16% comes from

cogeneration from natural gas, and 16% from renewables.⁴⁰ Therefore, generation of electricity from natural gas-fired generation systems is on the rise, while coal-fired electricity generation plants continue to be phased out.⁴¹

Table S8. Key input parameters and assumptions for the application of the Comparison Scenario in OSTUM and the CanmetENERGY model.

	OSTUM's Input Parameters/Assumptions	CanmetENERGY Model's Input Parameters/Assumptions
Feedstock	<ul style="list-style-type: none"> Type: Cold Lake (CL) dilbit blend Mass flow rate: 400,000 bpd 	
Technology	<ul style="list-style-type: none"> Upgrading technology: delayed coking-based Electricity generation technology: off-site natural gas-fired generation plant 	
Energy Inputs to Upgrader	<ul style="list-style-type: none"> Fuels: Natural gas is the only fuel consumed for heat, steam and hydrogen generation Energy inputs: <ul style="list-style-type: none"> Imported natural gas Imported electricity On-site generated steam On-site generated hydrogen 	
Products/By-products	<ul style="list-style-type: none"> Products/co-products: sweet SCO By-products: <ul style="list-style-type: none"> Fuel gas Coke Steam from waste heat 	
Disposition of By-products	<ul style="list-style-type: none"> Fuel gas: flared Coke: stockpiled Steam from waste heat: used in mining operations 	
Upgrading Emissions	<ul style="list-style-type: none"> GHGs: CO₂, CH₄, N₂O reported as CO₂ equivalents (CO₂e) Allocation method: none used, all emissions are assigned to SCO, the only product 	<ul style="list-style-type: none"> GHGs: CO₂ Allocation method: none available
Diluent Recovery Unit	<ul style="list-style-type: none"> NG consumption: 102.9 scf/bbl feed Steam consumption: 10.0 lb/bbl feed Electricity consumption: 0.7 kWh/bbl feed 	<ul style="list-style-type: none"> HYSYS built-in operating conditions
Vacuum Distillation Unit	<ul style="list-style-type: none"> NG consumption: 63.8 scf/bbl feed Steam consumption: 6.5 lb/bbl feed Electricity consumption: 0.3 kWh/bbl feed 	<ul style="list-style-type: none"> HYSYS built-in operating conditions
Delayed Coker	<ul style="list-style-type: none"> NG consumption: 136.9 scf/bbl feed Steam consumption: 20.0 lb/bbl feed Electricity consumption: 2.4 kWh/bbl feed Furnace outlet temperature: 482.2 °C 	<ul style="list-style-type: none"> Literature model implemented in HYSYS and adjusted with proprietary pilot plant data¹⁶ Furnace outlet temperature: 482.2 °C
Naphtha Hydrotreater	<ul style="list-style-type: none"> NG consumption: 18.9 scf/bbl feed Steam consumption: 3.5 lb/bbl feed Electricity consumption: 1.0 kWh/bbl feed Feed's bromine number: 80.0 g Br₂/100g feed Feed's diene number: 10.0 g I₂/100g feed Feed's aromatics content: 25.3 wt% Liquid hourly space velocity: 2.5 h⁻¹ Average catalyst bed temperature: 285.0 °C Reactor pressure: 4.0 MPa H₂/oil ratio: 1,680.0 scf/bbl feed 	<ul style="list-style-type: none"> Literature model implemented in HYSYS and adjusted with proprietary pilot plant data¹⁶ Liquid hourly space velocity: 2.5 h⁻¹ Reaction temperature: 285.0 °C Reaction pressure: 4.0 MPa H₂/oil ratio: 1,680.0 scf/bbl feed

Table S8. Continued.

	OSTUM's Input Parameters/Assumptions	CanmetENERGY Model's Input Parameters/Assumptions
LGO Hydrotreater	<ul style="list-style-type: none"> • NG consumption: 20.6 scf/bbl feed • Steam consumption: 5.0 lb/bbl feed • Electricity consumption: 2.5 kWh/bbl feed • Feed's aromatics content: 46.8 wt% • Liquid hourly space velocity: 2.0 h⁻¹ • Average catalyst bed temperature: 340.0 °C • Reactor pressure: 5.0 MPa • H₂/oil ratio: 1,680.0 scf/bbl feed 	<ul style="list-style-type: none"> • HYSYS built-in module, adjusted with proprietary pilot plant data • Liquid hourly space velocity: 2.0 h⁻¹ • Reaction temperature: 340.0 °C • Reaction pressure: 5.0 MPa • H₂/oil ratio: 1,680.0 scf/bbl feed
HGO Hydrotreater	<ul style="list-style-type: none"> • NG consumption: 37.8 scf/bbl feed • Steam consumption: 7.8 lb/bbl feed • Electricity consumption: 3.1 kWh/bbl feed • Feed's aromatics content: 60.7 wt% • Liquid hourly space velocity: 1.0 h⁻¹ • Average catalyst bed temperature: 370.0 °C • Reactor pressure: 9.0 MPa • H₂/oil ratio: 3,370.0 scf/bbl feed 	<ul style="list-style-type: none"> • HYSYS built-in module, adjusted with proprietary pilot plant data • Liquid hourly space velocity: 1.0 h⁻¹ • Reaction temperature: 370.0 °C • Reaction pressure: 9.0 MPa • H₂/oil ratio: 3,370.0 scf/bbl feed
Amine Treatment/ Regeneration Units	<ul style="list-style-type: none"> • Steam consumption: 500.0 MJ/ton feed • Electricity consumption: 13.0 kWh/ton feed 	<ul style="list-style-type: none"> • Not included
Claus Sulfur Recovery/ Claus Tail Gas Treatment	<ul style="list-style-type: none"> • NG consumption: 1,000.0 MJ/ton feed • Steam consumption: -7,912.9 MJ/ton feed • Electricity consumption: 65.0 kWh/ton feed • Sulfur recovery unit S yield: 90.0 mol% S feed • Tail gas treatment S yield: 95.0 mol% S feed 	<ul style="list-style-type: none"> • Not included
Steam Methane Reformer	<ul style="list-style-type: none"> • NG consumption as fuel: 0.04 scf/scf H₂ produced • NG consumption as feedstock: 0.34 scf/scf H₂ produced • Steam consumption: 1,793.6 MJ/ton feed • Electricity consumption: 0.001 kWh/scf H₂ produced 	<ul style="list-style-type: none"> • Emissions factor: 12 kg CO₂/kg H₂ produced
Boilers	<ul style="list-style-type: none"> • Fuel consumption: 3.5 MJ/kg steam produced • Steam consumption: 0.2 MJ/kg steam produced • Electricity consumption: 0.01 kWh/kg steam produced 	<ul style="list-style-type: none"> • HYSYS built-in operating conditions

The assay used to represent the properties of Cold Lake (CL) dilbit blend in the Comparison Scenario is presented in Table S9.

Table S9. Cold Lake dilbit blend assay used in Comparison Scenario.

		Cold Lake (CL) dilbit blend						
Initial Cut Point Temperature, °C		IBP	190 +	190	204	343	524 +	
End Cut Point Temperature, °C		190		204	343	524		
Property	Units	Full Crude	Diluent	ATB	Naphtha	LGO	HGO	VR
Volumetric Yield	LV%	100	27	73	0.5	11	23	38
Mass Yield	wt%	100	20	80	0.3	11	24	44
Sulfur Content	wt%	3.8	0.3	3.5	0.1	1.6	3.2	6.1
Nitrogen Content	mass ppm	3,715	48	1,979	18	76	1,563	7,085
API Gravity	°API	20	63	15	71	28	16	3
Specific Gravity @60/60 °F		0.9	0.7	1.0	0.7	0.9	1.0	1.1
Hydrogen Content	wt%	NA	15	11	15	12	11	9
MCRT Carbon	wt%	10	0.0	1.1	0.0	0.0	0.0	23.2
Characterization Factor, Kw		NA	12.2	11.4	12.4	11.3	11.3	11.1
Tb(50%) Weight Basis	°C	NA	114	457	91	280	437	599

Sensitivity and Scenario Analyses. As described in the Sensitivity and Scenario Analyses section of the manuscript, these analyses are developed to explore the effects on the Comparison Scenario's GHG emissions of changes in input parameter values and assumptions about fuels and electricity generation sources. For the Fuels Scenario, the amounts of fuel gas and coke required and consumed are determined by OSTUM in accordance with the other input parameters/assumptions in the Comparison Scenario. The amounts of by-products used differ somewhat from their average use by Suncor during the period 2008-2015 as reported by AER³⁹ (use of 54% of fuel gas production in the Fuels Scenario vs 66% reported by AER³⁹; 6% of coke production used in the Fuels Scenario vs 17%). The lower use of coke by OSTUM may be due to a portion of Suncor's 17% of coke production being directed to their mining operations. Currently, there is not enough public information to run a case that fully represents a specific delayed coking-based facility as the upgrading and mining operations are integrated and additionally, the operations generally have a large degree of variation in terms of operating conditions and practices. However, the ranges of possible input parameters

available in OSTUM and its flexibility in representing different scenarios facilitate the model to capture much of this variation. Work is currently underway to collect data from operators for further development of OSTUM.

The impact on upgrading GHG emissions when the electricity required by the Comparison Scenario upgrader is assumed to be generated by a coal-fired off-site system, an on-site cogeneration unit, the 2013 Alberta electricity grid mix and three additional scenarios combining off-site generated electricity and on-site cogeneration are also analyzed. For results of these analyses see; “Results: Sensitivity and Scenario Analyses” of this document, Table S11 on page S61.

Results: CanmetENERGY Model's Results for Comparison Scenario Application

Running the Comparison Scenario's set of conditions in CanmetENERGY's model resulted in total CO₂ emissions of 294 kg CO₂/m³ SCO (46 kg CO₂/bbl SCO). As expected, hydrogen production through steam reforming is the major source of CO₂ emissions (56% of emissions), while natural gas combustion to produce heat accounts for 34%. Steam generation emits 8% of total emissions, and the balance (2%) is emitted during the production of electricity. Emissions from hydrogen production are assigned to the naphtha, LGO, and HGO hydrotreaters consuming the hydrogen, and therefore account for the highest share of emissions (62%). Currently the model does not simulate a SMR, but accounts for its CO₂ emissions using an emissions factor of 12 kg CO₂/kg hydrogen.¹⁷ The model does not account for emissions generated by other secondary processes (e.g., amine treatment/regeneration, sulfur recovery), and does not breakdown emissions by direct/indirect sources. However, it provides estimates of chemical hydrogen consumption (Table 1 in the manuscript) and product yields at each upgrading step (Table S10).

Results: Comparison of OSTUM's Results with the CanmetENERGY Model for Comparison Scenario

Energy Use. When OSTUM and the CanmetENERGY model are run with consistent system boundaries, the natural gas and hydrogen inputs are in good agreement (differences within 12% and 7%, respectively). OSTUM's steam consumption is 41% higher than that calculated by the CanmetENERGY model because the latter does not account for steam consumption in hydrotreaters and SMR (which account for 30% of OSTUM's steam requirements). Similarly, OSTUM's electricity input is 2.6 times higher than CanmetENERGY's since it accounts for the electricity used in each process unit, while the CanmetENERGY model only accounts for the electricity consumed by the delayed coker.

Upgrading GHG Emissions. In terms of emissions intensity, the difference between OSTUM's GHG emissions for the delayed coking-based upgrading plant (268 kg CO₂e/m³ SCO) and CanmetENERGY's (294 kg CO₂/m³ SCO) is within 9%. OSTUM's direct emissions from natural gas combustion for heat generation are 4% higher than those calculated by CanmetENERGY's model. The difference mainly arises from the different calculation approaches: CanmetENERGY's model uses HYSYS built-in modules and literature models adjusted with proprietary pilot plant data, while OSTUM uses energy use factors from the public literature. OSTUM's direct emissions from natural gas steam generation are similar (difference within 4%) to CanmetENERGY's. Direct emissions from hydrogen production are 26% lower in OSTUM than in CanmetENERGY's model. In OSTUM, these emissions are directly related to hydrogen consumption levels, which are 7% lower than in CanmetENERGY's model. The main

reasons for this discrepancy are differences in the hydrogen consumption estimation methods and in the emissions factors used by the models. While both models use the same literature kinetic model¹⁸ to represent the hydrotreating reactions in the naphtha hydrotreater (although implemented in different software), OSTUM's hydrotreating reactions in the LGO and HGO hydrotreaters are simulated using kinetic models proposed in Yui and Sanford,¹⁹ while the CanmetENERGY model uses HYSYS's built-in gasoil hydrotreating module. OSTUM also uses correlations from Edgar^{25,26} to calculate chemical hydrogen consumption and a hydrogen production emissions factor of 11 kg CO₂e/kg hydrogen produced, while CanmetENERGY model's corresponding emissions factor is slightly higher (12 kg CO₂/kg hydrogen produced).¹⁷ Finally, electricity consumption indirect emissions are 3.8 times higher in OSTUM than in CanmetENERGY's model, since the latter accounts only for electricity consumed by the delayed coker. Electricity emissions from OSTUM's delayed coker are 4 kg CO₂e/m³ SCO, which are close to CanmetENERGY's 5 kg CO₂/m³ SCO.

Both models are capable of calculating the emissions intensity of each process unit. OSTUM assigns all emissions from steam production to boilers, while the CanmetENERGY model distributes these emissions among the process units consuming steam. When direct emissions from generation of the steam consumed by OSTUM's diluent recovery (8 kg CO₂e/m³ SCO) and vacuum distillation (4 kg CO₂e/m³ SCO) are assigned to these units, their emissions intensities are of the same magnitude as those of CanmetENERGY. OSTUM's emissions for the delayed coker are 21% higher than those of CanmetENERGY. When accounting for emissions from the steam consumed by the delayed coker (6 kg CO₂e/m³ SCO), OSTUM's emissions are 53% higher than

CanmetENERGY's ($29 \text{ kg CO}_2\text{e/m}^3 \text{ SCO}$ vs. $19 \text{ kg CO}_2\text{e/m}^3 \text{ SCO}$). This discrepancy mainly arises from OSTUM's application of literature energy use factors, which are of different magnitude than the ones obtained by CanmetENERGY's model from literature and thermodynamic/energy balance calculations. The delayed coker's emissions represent 9% and 6% of the plants' emissions in OSTUM and the CanmetENERGY model, respectively, and therefore this is an area of ongoing investigation. The process units that produce hydrogen (SMR) and consume it (hydrotreaters) reflect the aforementioned difference in emission intensities from hydrogen production.

OSTUM calculates emissions from process units not included in CanmetENERGY's model (e.g., sulfur recovery/tail gas treatment, amine fuel gas treatment/amine regeneration). These units are responsible for $5 \text{ kg CO}_2\text{e/m}^3 \text{ SCO}$ or 2% of upgrading emissions. Although the contribution is relatively small, they add completeness to the modeling of upgrading emissions. OSTUM also estimates indirect emissions from the use of natural gas ($48 \text{ kg CO}_2\text{e/m}^3 \text{ SCO}$), which represent 15% of total upgrading emissions. This contribution to emissions is important and therefore should be included in the modeling of life cycle emissions from upgrading.

The comparison between OSTUM and the CanmetENERGY model elucidates key differences between them. OSTUM is a tool incorporating life cycle methods that is developed with accessible spreadsheet-based software and literature input data. It accounts for the energy consumed in upgrading operations to estimate their GHG emissions. CanmetENERGY's process simulation model is developed with proprietary software, using public and proprietary pilot plant data, and evaluates upgrading energy

intensity and CO₂ emissions with a strong focus on the analysis of product yield/quality to help improve process efficiency and inform life cycle models.¹⁷ While the upgrading emissions calculated by the models are similar (difference within 9%), the input data and methods employed to obtain them are distinct, suggesting the dependability and consilience of the models.

Product Yields. The product yields calculated by OSTUM for the feedstock separation, primary and secondary upgrading stages, and the overall product yield of the Comparison Scenario are presented in Table S10. The product yields at every upgrading stage as calculated by the CanmetENERGY model for the same Comparison Scenario are also presented.

Table S10. Comparison Scenario product yields calculated by OSTUM and the CanmetENERGY model.

Process Units	Products	OSTUM Product Yields, wt%	CanmetENERGY's Model Product Yields, wt%
Diluent Recovery Unit	Diluent	20.5	23.2
	ATB	79.5	76.8
Vacuum Distillation Unit	Naphtha	0.3	0.4
	LGO	10.9	11.1
	HGO	24.3	23.3
	VR	44.0	42.0
Delayed Coker	H ₂ S		1.5
	NH ₃	10.1	0.1
	Gas (C1-C4)		6.1
	Naphtha (IBP-204 °C)	16.4	15.5
	LGO (204-343 °C)	18.1	20.8
	HGO (343-524 °C)	23.9	23.5
	VR (524 °C+)	0.0	1.5
	Coke	31.5	31.0
	Total	100.0	100.00
Naphtha Hydrotreater	H ₂ S	1.5	1.7
	NH ₃	0.04	0.03
	Gas (C1-C4)	0.0	0.04
	Naphtha (IBP-204 °C)	99.6	97.0
	LGO (204-343 °C)	0.0	2.4
	HGO (343-524 °C)	0.0	0.0
	Total	101.1	101.2
LGO Hydrotreater	H ₂ S	2.5	2.8
	NH ₃	0.1	0.1
	Gas (C1-C4)	0.2	0.2
	Naphtha (IBP-204 °C)	8.1	8.1
	LGO (204-343 °C)	90.4	90.3
	HGO (343-524 °C)	0.00	0.0
	Total	101.3	101.4
HGO Hydrotreater	H ₂ S	3.6	3.8
	NH ₃	0.2	0.2
	Gas (C1-C4)	0.2	0.2
	Naphtha (IBP-204 °C)	1.4	1.7
	LGO (204-343 °C)	9.3	9.4
	HGO (343-524 °C)	86.8	86.4
	Total	101.5	101.7
Overall Product Yield (based on ATB feed)	Sour Gases (H ₂ S+NH ₃ +C1-C4)	8.1	7.0
	Naphtha (IBP-204 °C)	12.0	11.6
	LGO (204-343 °C)	25.5	27.7
	HGO (343-524 °C)	38.0	37.9
	Coke	17.4	17.0
	Total	101.1	101.2
SCO Yield		75.5	77.2

ATB: atmospheric topped bitumen; LGO: light gas oil; HGO: heavy gas oil; VR: vacuum residue; H₂S: hydrogen sulfide; NH₃: ammonia; gas (C1-C4): alkane gases, specifically methane, ethane, propane, and butanes; IBP: initial boiling point; SCO: synthetic crude oil.

The overall product yield predicted by OSTUM for the Comparison Scenario is very similar to the one calculated by the CanmetENERGY model (0.1% difference). The

difference in product yields from the DRU between the two models is within 12%, and within 5% for most of the vacuum distillation unit's products except for naphtha. The difference between naphtha yield estimates (29%) is mainly due to the calculation methods. CanmetENERGY's model employs HYSYS's rigorous thermodynamic calculations to solve the vacuum distillation column, producing realistic product yields with 5-10% overlapping between fractions, while OSTUM assumes perfect fractionation with exact boiling ranges and no overlapping. OSTUM's delayed coker product yields are calculated using a set of linear empirical correlations³⁰ that do not account for the estimation of individual gaseous species (H_2S , NH_3 , C1-C4) nor unconverted residue (vacuum residue, VR). Therefore, the biggest difference between OSTUM and CanmetENERGY's delayed coker product yields is related to these fractions. The coker gas yield in OSTUM is 31% higher than CanmetENERGY's estimate (obtained implementing a literature kinetic model in HYSYS¹⁶). However, the yields predicted for the rest of the delayed coker products compare well (difference within 14%) with the product distribution calculated by CanmetENERGY's model. OSTUM's calculation of the product yields in the naphtha hydrotreater derives from the assumption that hydrocracking reactions are minimal in this unit and can be assumed to be negligible. Therefore, the entire liquid product is assumed to be hydrotreated naphtha (since there is negligible formation of LGO and HGO products), while H_2S/NH_3 yields are calculated from the conversion levels of sulfur and nitrogen calculated by the Yui kinetic model.¹⁸ The CanmetENERGY model predicts with more detail the distribution of products in the naphtha hydrotreater through the implementation of a literature kinetic model¹⁶ in HYSYS. However, the yield of total liquid product from the naphtha hydrotreaters is very similar for the two models (0.2% difference). Since mild hydrocracking reactions in the

LGO and HGO hydrotreaters produce additional amounts of naphtha and LGO, a literature kinetic model simulating mild hydrocracking of bitumen-derived gas oils²³ is implemented in OSTUM to calculate the LGO and HGO hydrotreaters product yields. Even though the CanmetENERGY model uses HYSYS built-in modules to calculate the product yields from the LGO and HGO hydrotreating units, the product distributions predicted by both models are very similar (difference between product yields is less than 5% for all products, except for the H₂S yield in LGO hydrotreaters (11%) and the naphtha yield in HGO hydrotreaters (19%)). Finally, the yield of SCO predicted by both models is consistent (2% difference).

Results: Comparison of OSTUM's Results with Other Literature

OSTUM's Comparison Scenario delayed coking-based upgrading emissions in Figure 2 of the manuscript (represented by a stacked bar) are obtained running the model under the Comparison Scenario's set of conditions. The lower and upper emissions estimates result from alternative scenarios run assuming the Comparison Scenario's set of conditions but varying the SMR's natural gas consumption as feedstock. OSTUM's upgrading emissions were found to be most sensitive to changes in this parameter (see SI "Results: Sensitivity and Scenario Analyses"). For Figure 2, the natural gas consumption for hydrogen production was varied by +/-20%. Hydrogen consumption does not change drastically under normal operating conditions but can realistically vary within this range due to changes in bitumen feedstock properties, variation in operating conditions (e.g., temperature, pressure) and/or through deactivation of catalysts in the upgrading operation. Studies examining other upgrading technologies, e.g., hydroconversion, are excluded from the comparison.

Delayed coking-based upgrading emissions from CanmetENERGY are obtained running the Comparison Scenario in the CanmetENERGY model, as discussed (see previous sections in SI "Methods: Application of Comparison Scenario in OSTUM and CanmetENERGY Models", and "Results: CanmetENERGY Model's Results for Comparison Scenario Application"). Emissions from the Greenhouse Gas Emissions of Current Oil Sands Technologies (GHOST) model²¹ are obtained running its upgrading module for a delayed coking-based upgrading scenario, using the model's default input parameters. GHOST's result (349 kg CO₂e/m³ SCO) is 6% higher than OSTUM's Comparison Scenario estimate (328 kg CO₂e/m³ SCO). GHOST is based on confidential

oil sands project operating data; therefore, the similarity between OSTUM and GHOST's results highlights the former's advantage of estimating emissions consistent with the industry while analyzing upgrading emissions sources and the sensitivity of emissions to energy inputs, operating conditions, etc. OSTUM's delayed coking-based upgrading emissions are also compared with studies^{42,43} performed by Jacobs Consultancy that have been considered reliable references for project-specific life cycle upgrading emissions.⁴⁴ Both reports calculate the GHG emissions from delayed coking-based upgrading projects simulated in proprietary refinery software and using confidential data. Jacobs 2012⁴³ emissions estimate is 21% lower than OSTUM's Comparison Scenario emissions result. This study does not provide details on the calculation method/assumptions for its delayed coking-based upgrading emissions estimate, which is based on confidential operating data for a single year from an oil sands company. The study clarifies it is a preliminary estimate that has not been reviewed with other industry/government stakeholders, and therefore it should not be considered as an industry benchmark.⁴³ On the other hand, Jacobs 2009⁴² delayed coking-based upgrading emissions estimate is 6% lower than OSTUM's Comparison Scenario estimate. This earlier report by Jacobs Consultancy details the key assumptions and methodology used to calculate its upgrading emissions results, and therefore the difference in delayed coking-based upgrading emissions estimates is expected due to the use of different data sources, assumptions, modeling techniques, and modeling software. A study by Ordorica-Garcia et al.³⁸ calculates delayed coking-based upgrading emissions using the Oil Sands Operations Model (OSOM) for a base case scenario run in Aspen Plus using refining literature data to model some of the process units. The study's delayed coking-based upgrading emissions estimate is the closest to OSTUM's Comparison Scenario emissions (only 3% difference between both

models' emissions estimates). The delayed coking-based upgrading emissions estimated by the FUNNEL-GHG-OS model⁴⁵ are 20% lower than OSTUM's Comparison Scenario emissions estimate. The values assumed by the FUNNEL-GHG-OS model for hydrogen demand of the naphtha, LGO, and HGO hydrotreaters are 71%, 23%, and 10% lower, respectively, than their counterparts in OSTUM's Comparison Scenario. The FUNNEL-GHG-OS model does not calculate the upgrader's hydrogen demands, a critical parameter in the estimation of upgrading emissions because the production of this hydrogen generates the largest share of emissions. Rather, the model assumes literature values of hydrogen consumption for each of the hydroprocessing units. However, hydrogen consumption values for oil sands hydroprocessing units are scarce in the literature. Most hydrogen consumption values in the literature refer to the hydrogen demand of refineries' hydroprocessing units. Literature values related to hydroprocessing of bitumen-derived fractions are either point estimates that apply for a particular combination of feedstock and process, or are wide ranges of possible values from which it is difficult to select appropriate/representative values for each hydroprocessing unit. Since the FUNNEL-GHG-OS model⁴⁵ does not account for the quality of feedstocks/products nor the operating conditions of each hydroprocessing unit, it is not possible to determine if the literature values assumed for hydrogen consumption are representative.

OSTUM's Energy Efficiency of Process Units Compared With Those of Elgowainy et al. Elgowainy et al.⁴⁶ propose a methodology for allocating overall refinery energy use and GHG emissions among various refinery products at the process unit level. The method calculates the energy burden of each refinery input that contributes to the production of a unit of energy of each refining product. The sum of all energy burdens for a particular product stream is defined as the total energy intensity of the product stream

(i.e., the share of the total amount of refinery input energies required to produce the unit energy of that stream). The energy efficiency of a product is the inverse of its energy intensity. Therefore, for a given process unit, the energy burden ($EI_{i,j}$ in Btu/Btu) of a refinery input i to produce the unit energy of a given product yield stream j can be expressed using the equation:

$$EI_{i,j} = (\sum F_k \times EI_{i,k}) \times S_j \div Y_j \quad (26)$$

where F_k and Y_j are the energy in feed k and product yield stream j to and from the process unit (in Btu/day), respectively, while S_j is the percentage contribution of product yield j in all product yield streams from a given process unit. Common metrics for allocating the energy burdens to a product yield stream by its share (S_j) are energy, market value, and mass allocations. The authors adopted the energy basis allocation.

OSTUM includes a very similar allocation methodology that distributes energy and emissions to upgrading products at the process unit level based either on a hydrogen content, energy, or mass basis. Therefore, the energy basis allocation method was applied to OSTUM's Comparison Scenario for comparison with the method of Elgowainy et al. The energy intensity of each process unit was calculated by adding the total energy input to a process unit with its upstream burden (up to the upgrader gate) and then dividing by the total energy output of that process unit. Figure S3 presents the energy intensities of each process unit calculated by OSTUM (process units from utility plants are not included since no energy/emissions are allocated to them). The range of energy intensities reported by Elgowainy et al.⁴⁶ for similar process units in 43 U.S. refineries is also included for comparison.

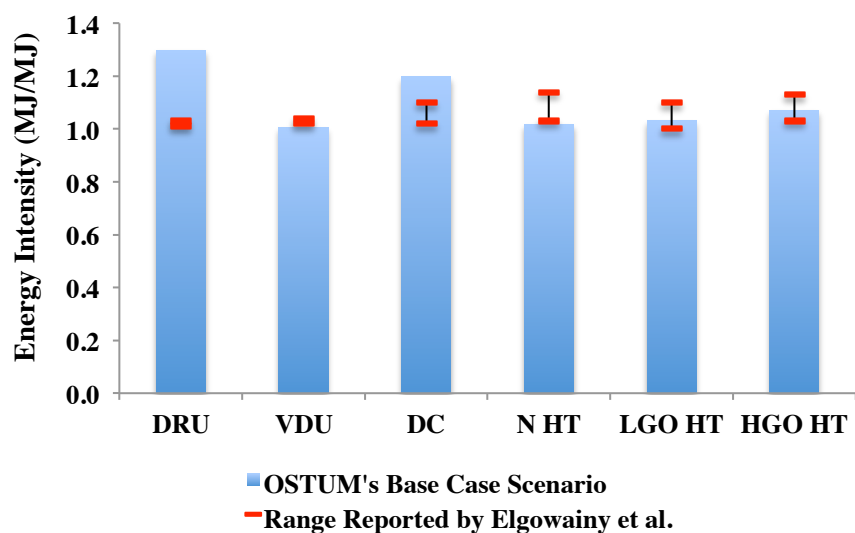


Figure S3. Comparison of energy intensities of process units relevant to the bitumen upgrading process as calculated by OSTUM's Comparison Scenario and as reported by the Elgowainy et al.⁴⁶ study of 43 U.S. refineries.

Abbreviations: DRU: diluent recovery unit (atmospheric distillation); VDU: vacuum distillation; DC: delayed coker; N HT: naphtha hydrotreater; LGO HT: light gas oil hydrotreater; HGO HT: heavy gas oil hydrotreater.

The energy intensities of OSTUM and Elgowainy et al. are similar. The difference in energy intensities estimated for the DRU (atmospheric distillation) is the largest (average percentage difference between OSTUM's Comparison Scenario value and range of values from Elgowainy et al. is 24%). For the rest of the process units compared, the average percentage difference between estimates is 6%. Examining sources of differences, particularly for the DRU, will continue in future work.

Results: Comparison of OSTUM's Results with Confidential Commercial Upgrading Operating Data

OSTUM's input data and calculation methods are tested against upgrading energy use data and GHG inventory results provided by an oil sands company under a non-disclosure agreement. The energy use data and GHG emissions intensities reported by the company were not used in the development of OSTUM or in any of OSTUM's scenarios; therefore, these are completely independent of the model. The energy input data and GHG emissions provided by the company correspond to a current major delayed coking-based upgrading project operating in the Athabasca region.

Comparison Scenario emissions calculated by OSTUM are similar to those provided by the oil sands company for its delayed coking-based upgrading operations (6% deviation). The total consumption of natural gas calculated by OSTUM for the Comparison Scenario compares quite closely to the total fuel input reported by the company for its upgrading operations (1% deviation between estimates). However, the difference between the electricity input calculated by OSTUM and the one reported by the company is 22%. The reason for this difference might be related to the process units included in each assessment and/or the data sources used to calculate the electricity use estimates. The electricity consumption calculated by OSTUM for the Comparison Scenario takes into account the electricity consumed by the distillation units, delayed coker, hydrotreaters, steam methane reformer, boilers, amine treatment/regeneration units, and sulfur recovery units. When the electricity consumed by secondary process units like the amine treatment/regeneration unit and the sulfur recovery unit is excluded from the analysis (like in the Comparison Scenario vs. the CanmetENERGY model), the difference

between electricity consumption estimates reduces to 7%. Another possible explanation for this discrepancy is that, although a considerable effort was made to find literature electricity consumption factors for each of OSTUM's process units that are representative of current oil sands upgrading operations, it is possible that some of OSTUM's process units use electricity consumption factors of higher magnitude than the electricity actually consumed by these units in commercial operations. In any case, since GHG emissions from electricity consumption constitute only a small fraction of the total emissions generated by an oil sands upgrader (e.g., 7% for the Comparison Scenario), the difference in electricity consumption estimates between OSTUM and the oil sands company does not have a significant effect on overall upgrading emissions.

Results: Sensitivity and Scenario Analyses

Table S11 presents results for the sensitivity (top portion of table) and scenario (bottom portion of table) analyses of OSTUM based on varying values of parameters from their values in the Comparison Scenario. The table presents the key input parameters employed in the sensitivity analysis, their values for the Comparison Scenario and lower and upper values in the sensitivity analysis. A positive (negative) percent deviation represents an increase (decrease) in upgrading emissions with respect to the Comparison Scenario emissions. Figure S4a presents the sensitivity analysis results in the form of a tornado plot.

The results for the scenario analysis are shown in the bottom portion of the table by scenario, and as well presented in Figure S4b. Only those scenarios resulting in emissions deviations greater than 1% are presented.

Table S11. Results of sensitivity and scenario analyses: Effect on Comparison Scenario upgrading GHG emissions of variations in key input parameters and energy inputs.

Input Parameter / Scenario	Variation in Input Parameter / Scenario	Input Parameter Value	Upgrading GHG Emissions (kg CO ₂ e/m ³ SCO)	% Increase or Decrease in Emissions from Comparison Scenario
SENSITIVITY ANALYSIS				
Steam Methane Reformer				
Natural gas consumed as feedstock (scf/scf H)	Comparison Scenario	0.34	328	0
	50% increase	0.51	393	20
	50% decrease	0.17	263	-20
Natural gas consumed as fuel (scf/scf H)	Comparison Scenario	0.04	328	0
	50% increase	0.06	335	2
	50% decrease	0.02	321	-2
Steam consumed (MJ/ton feed)	Comparison Scenario	1,793.6	328	0
	50% increase	2,690.4	331	1
	50% decrease	896.8	325	-1
Diluent Recovery Unit and Vacuum Distillation Unit				
Natural gas consumed in DRU (scf/bbl feed)	Comparison Scenario	102.9	328	0
	50% increase	154.4	354	8
	50% decrease	51.5	303	-8
Natural gas consumed in VDU (scf/bbl feed)	Comparison Scenario	63.8	328	0
	50% increase	95.7	344	5
	50% decrease	31.9	312	-5
Steam consumed in DRU (lb/bbl feed)	Comparison Scenario	10.0	328	0
	50% increase	15.0	332	1
	50% decrease	5.0	324	-1
Delayed Coker				
Natural gas consumed (scf/bbl feed)	Comparison Scenario	136.9	328	0
	50% increase	205.4	346	5
	50% decrease	68.5	311	-5
Hydrotreaters				
Hydrogen consumed by naphtha HT (scf/bbl feed)	Comparison Scenario	556.3	328	0
	25% increase	695.4	331	1
	25% decrease	417.2	325	-1
Hydrogen consumed by LGO HT (scf/bbl feed)	Comparison Scenario	738.7	328	0
	25% increase	923.4	338	3
	25% decrease	554.1	319	-3
Hydrogen consumed by HGO HT (scf/bbl feed)	Comparison Scenario	962.4	328	0
	25% increase	1,203.0	349	6
	25% decrease	721.8	307	-6
SCENARIO ANALYSIS				
Use of By-products/Cogeneration as Energy Inputs				
Use of by-products/cogeneration	Comparison Scenario	0% used	328	0
	Fuel gas use	66% used	297	-9
	Coke use	8% used	344	5
	Fuels Scenario	54% of fuel gas production used; 6% of coke production used; 70% of electricity cogenerated	309	-6

Table S11. Continued.

Input Parameter / Scenario	Variation in Input Parameter / Scenario	Input Parameter Value	Upgrading GHG Emissions (kg CO ₂ e/m ³ SCO)	% Increase or Decrease in Emissions from Comparison Scenario
Electricity Generation System				
Type of electricity generation system	Comparison Scenario: off-site natural gas-fired generation	100%	328	0
	Off-site coal-fired generation	100%	351	7
	2013's Alberta's Electricity Generation Mix	100%	337	3
	Cogeneration	100%	312	-5
	50% of Electricity Generated w/ Coal + 50% from Cogeneration	50% from coal/ 50% from cogen	333	1
	50% of Electricity Generated w/ Natural Gas + 50% from Cogeneration	50% from natural gas/ 50% from cogen	321	-2
	50% Electricity Generated w/ 2013's Alberta's Electricity Generation Mix + 50% from Cogeneration	50% from grid / 50% from cogen	326	-1

Abbreviations: H: hydrogen; DRU: diluent recovery unit; VDU: vacuum distillation unit; LGO: light gas oil; HGO: heavy gas oil; HT: hydrotreater

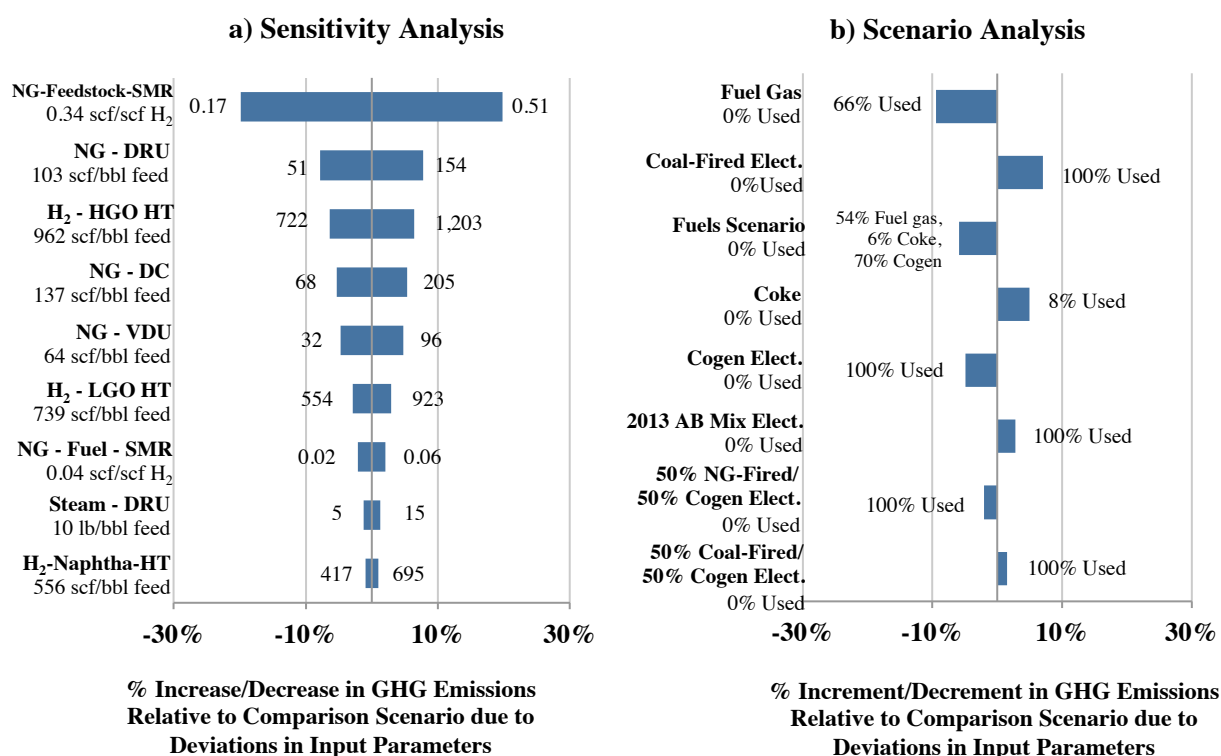


Figure S4. a) Sensitivity of OSTUM's Comparison Scenario GHG emissions results to selected input parameters, b) Variation in OSTUM's Comparison Scenario GHG emissions results for scenarios using by-products as energy inputs and different electricity generation sources.

Notes: The input parameters/scenarios and their Comparison Scenario values are listed on the y-axes while the ranges of variation for each parameter/scenario (in the same units as its corresponding Comparison Scenario value) are reported within the figure. Abbreviations: NG: natural gas; SMR: steam methane reformer; H₂: hydrogen gas; DRU: diluent recovery unit; DC: delayed coker; VDU: vacuum distillation unit; HGO: heavy gas oil; LGO: light gas oil; HT: hydrotreater; Elect.: Electricity; Cogen: cogeneration; AB: Alberta.

Figure S5 presents an additional plot of the sensitivity and scenario analyses results from Table S11. The upgrading emissions calculated by OSTUM (data markers) when key input parameters/energy input assumptions are changed from the Comparison Scenario values/assumptions are presented on the y-axis, while the x-axis lists the process

units/energy input scenarios associated with the list of variations displayed by the plot legend.

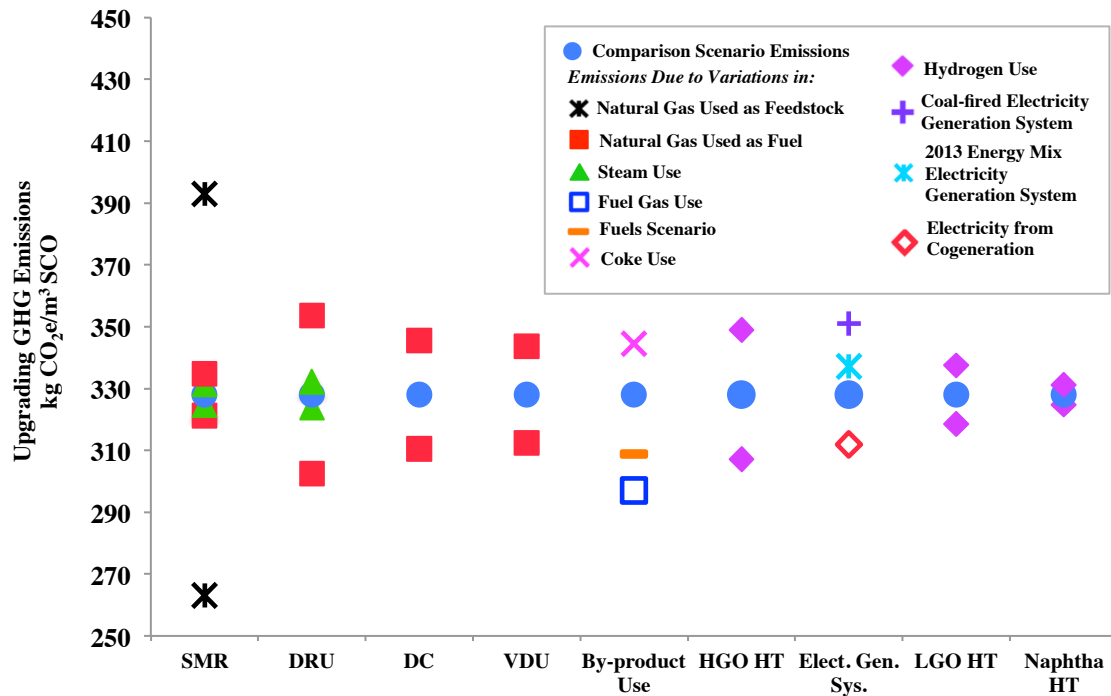


Figure S5. Deviations in upgrading GHG emissions due to $\pm 50\%$ variations from the Comparison Scenario values of key input parameters and energy input assumptions (denoted by the data markers).

Notes: The process units and energy input assumptions associated with each input parameter are listed on the x-axis. The input parameters associated with the three hydrotreaters are varied by $\pm 25\%$. Abbreviations: SMR: steam methane reformer; DRU: diluent recovery unit; DC: delayed coker; VDU: vacuum distillation unit; HGO: heavy gas oil; HT: hydrotreater; Elect. Gen. Sys.: type of electricity generation system; LGO: light gas oil.

OSTUM's upgrading emissions estimates are most sensitive to variations in the value of the SMR's input parameter describing the quantity of natural gas feedstock required for the reaction of natural gas and steam to produce a unit quantity of product hydrogen.

Upgrading emissions change by as much as $\pm 20\%$ when this parameter is varied $\pm 50\%$

from its Comparison Scenario value. Since the amount of natural gas consumed as fuel in the SMR is significantly lower than its consumption as feedstock, a $\pm 50\%$ variation in the amount of fuel used has an effect on final emissions ($\pm 2\%$) 10 times smaller than that caused by similar variations in the amount of natural gas feedstock used. On the other hand, the impact on upgrading emissions of variations in the steam consumption of the SMR was found to be even smaller ($\pm 1\%$). Steam consumption in this process unit is affected by plant economics.⁴⁷ Since the catalysts used in the reforming reactions require steam to be present in excess (increasing the volumetric throughput and cost of the plant), a reduction in the steam-to-carbon ratio is usually sought.⁴⁷ In doing so, there is an increase in natural gas feedstock consumption and an increase in the primary reformer radiant duty (the primary reformer is a large fired heater), which increases the steam generated in the reformer's convection section and decreases the amount of process steam injected to the reforming reactions.⁴⁷ The fuel demand for diluent recovery also has a considerable impact on emissions ($\pm 8\%$ change). The DRU might consume similar¹⁰ or higher amounts¹¹ of energy than vacuum distillation units (VDUs). In this study's Comparison Scenario, the DRU's energy intensity is higher than the VDU's. Therefore, a variation in the DRUs' fuel requirements has a greater impact on total energy demand and upgrading emissions than a similar variation associated with the VDU. Fuel use in the delayed coker (DC) and VDU have smaller impacts ($\pm 5\%$ change). Although the DC has higher fuel consumption than the DRU, its lower volumetric feed flow rate reduces its impact on upgrading emissions and makes it very similar to that of the VDU.

The impact on upgrading GHG emissions of a different energy inputs is also explored. First, the effect on emissions of individually using upgrading by-products fuel gas and

coke as energy inputs is examined. A scenario where fuel gas is the only by-product used as a substitute for all natural gas required by the upgrader's process heaters and a small fraction of the SMR's natural gas needs as feedstock results in a reduction of upgrading emissions of 9% compared to the Comparison Scenario. The use of fuel gas in oil sands upgraders is common. Upgraders burn the majority of this by-product as a fuel to run their operations and decrease the demand for natural gas. However, some upgrading operations treat small amounts of fuel gas as a waste stream and flare it.³⁹ The volumes of fuel gas produced, consumed and flared/wasted estimated by OSTUM in the scenario where the only by-product used is fuel gas are compared with those in AER's ST39 Statistical Report³⁹ for Suncor and CNRL (Table S12). While the AER data reported by these projects are for integrated (surface mining and upgrading) operations as discussed in the manuscript, because fuel gas is only produced by the upgrading operation and not in mining/extraction operations and can reasonably be assumed to be used primarily by the upgrading operation, this is a reasonable comparison and represents an additional evaluation step for OSTUM. OSTUM's estimates of produced fuel gas, used as fuel, and flared/wasted closely match those of Suncor as reported in AER ST39,³⁹ while the amounts of fuel gas produced and used as fuel reported for CNRL are higher than those estimated by OSTUM. This may result due to OSTUM's simulation of the delayed coker and hydroprocessing units' operating conditions being more similar to those of Suncor's operations.

Table S12. Comparison of fuel gas produced, used, and flared estimated by OSTUM's scenario analysis and average values reported by AER's ST39³⁹ for Suncor and CNRL for 2008-2014.

	OSTUM Scenario Analysis (m ³ /m ³ SCO)	Suncor Average for 2008-2014 reported in ST39 ³⁹ (m ³ /m ³ SCO)	CNRL Average for 2008-2014 reported in ST39 ³⁹ (m ³ /m ³ SCO)
Fuel Gas Produced	74	78	95
Fuel Gas Used as Fuel	48	51	90
Fuel Gas Flared/Wasted	2	4	2

Currently, the upgrading industry stockpiles the majority of its by-product coke; however, Suncor uses a fraction of its coke as fuel for steam generation and Syncrude uses some of its coke as fuel for fluid coking.⁴⁸ Table S13 presents a comparison of the amounts of coke produced, used as fuel, and stockpiled estimated by OSTUM in its scenario where the only by-product consumed is coke, with the average values reported by AER's ST39³⁹ for Suncor. However, the comparison between coke produced/used/stockpiled estimated by OSTUM and the amounts reported in AER ST39³⁹ is not straightforward because Suncor may consume some of its coke in its mining (as well as in its upgrading) operations and CNRL does not burn coke as a fuel.

Table S13. Comparison of coke produced, used, and stockpiled estimated by OSTUM's scenario analysis and average values reported by AER's ST39³⁹ for Suncor for 2008-2014.

	OSTUM Scenario Analysis (kg/m ³ SCO)	Suncor Average for 2008-2014 reported in ST39 ³⁹ (kg/m ³ SCO)
Coke Produced	199	247
Coke Used as Fuel	15	45
Coke Deliveries	NA	36
Coke Stockpiled	184	166

Abbreviations: NA: not available in OSTUM

OSTUM calculates that 8% of the coke produced (or 15 kg/m³ SCO) is needed to generate the steam required by the upgrader whereas Suncor's average use of coke as fuel

in the period 2008-2014 was 18% of its coke production; however, there is great month-to-month variability in Suncor's use of coke and in several months of 2013/14 5-9% of its coke production was used as fuel.

Table S11 shows that the use of electricity produced entirely from on-site cogeneration generates the lowest amount of emissions (5% decrease with respect to those estimated by the Comparison Scenario). A decrease in upgrading emissions of 1-2% is obtained when 50% of the upgrader's electricity requirements are met with grid electricity generated using either 2013 Alberta's electricity generation mix or natural gas-fired generation systems, and 50% with electricity produced on-site through cogeneration. However, when 50% of the electricity requirements are met using a coal-fired generation system and 50% with on-site cogeneration, there is a slight increase in emissions (1%). The use of electricity exclusively from the grid generated by off-site systems burning fuels other than natural gas results in an increase in upgrading emissions of 3-7% with respect to those of the Comparison Scenario.

Finally, the sensitivity analysis shows that the amount of hydrogen consumed by the hydrotreating units also has an important impact on upgrading emissions. Total emissions change by $\pm 6\%$, $\pm 3\%$, and $\pm 1\%$ when the hydrogen consumption of the HGO, LGO, and naphtha hydrotreaters (respectively) vary by $\pm 25\%$ of the Comparison Scenario values.

Hydrotreaters use hydrogen and catalysts to improve the quality of the downstream product, chemically saturating and stabilizing the crude fractions processed and removing from them unwanted species (e.g., sulfur, nitrogen, dissolved metals, and oxygen) to meet environmental restrictions and protect/improve the performance of refinery catalysts.⁴⁹

Hydrogen consumption in hydrotreaters is mainly determined by feedstock properties, the level of conversion/removal of impurities, and the properties of the catalysts.²⁶ Therefore,

variability in hydrogen consumption is mainly due to the levels of aromatics, olefins, diolefins, sulfur, nitrogen, and other impurities on the feedstock; the desired extent of hydrogenation; the severity of the operating conditions to achieve a certain degree of conversion, and the activity of the catalysts.⁵⁰ As a feed becomes heavier, the number of impurities species and their concentration increases, requiring substantially more addition of hydrogen to reach the product quality desired.²⁶ This way, the average hydrogen demand for hydrotreating HGO is higher than the average hydrogen requirements for the hydrotreating of the LGO and naphtha fractions. In typical diluted bitumen feedstocks, the bitumen fraction is mainly composed of HGO and VTB (vacuum-topped bitumen), while LGO comprise a small amount, and naphtha even a smaller amount.¹⁶ VTB fed to a delayed coker/hydroconverter is mainly composed of HGO and LGO fractions with high concentration of carbon and impurities.¹⁶ Therefore, the HGO and LGO hydrotreaters typically processes higher feed flow rates, and a variation in their hydrogen consumption has greater impact on upgrading emissions than variations in the hydrogen consumed by the naphtha hydrotreating unit.

Hydrogen consumption data for heavy oil/bitumen-derived hydrotreating units found in the literature^{50,26,51,13} vary widely, usually in the range of (400-1,000 scf/bbl),¹³ for heavy oil and (592-1,036 scf/bbl,²⁶ 600-1,200 scf/bbl),¹³ for VR (vacuum residue). This is because is very difficult to determine ‘typical’ ranges of hydrogen consumption for hydrotreaters processing bitumen-derived fractions, due to the variability in the quality of feedstocks, the desired level of impurities removal, etc. Therefore, the ranges of chemical hydrogen consumption calculated by OSTUM for each hydrotreater in Figure S1 (obtained when the temperature of the hydrotreating reactors is varied within $\pm 40^{\circ}\text{C}$ from the Comparison Scenario temperatures to produce a range of sulfur conversion of 85-

100%) can be used to analyze in more detail the impact of hydrogen consumption in upgrading emissions. Figure S6 presents the variations in upgrading emissions obtained when OSTUM's Comparison Scenario is run for the aforementioned ranges of chemical hydrogen consumption in each of the hydrotreating units. The variation in hydrogen consumption values is performed one at the time and the upgrading emissions calculated by the model are registered under each hydrogen use assumption. A range of 406-618 scf/bbl is assumed for the chemical hydrogen consumption in the naphtha hydrotreater; 507-834 scf/bbl is assumed for the LGO hydrotreater, and 641-1,139 scf/bbl is used for the HGO hydrotreater.

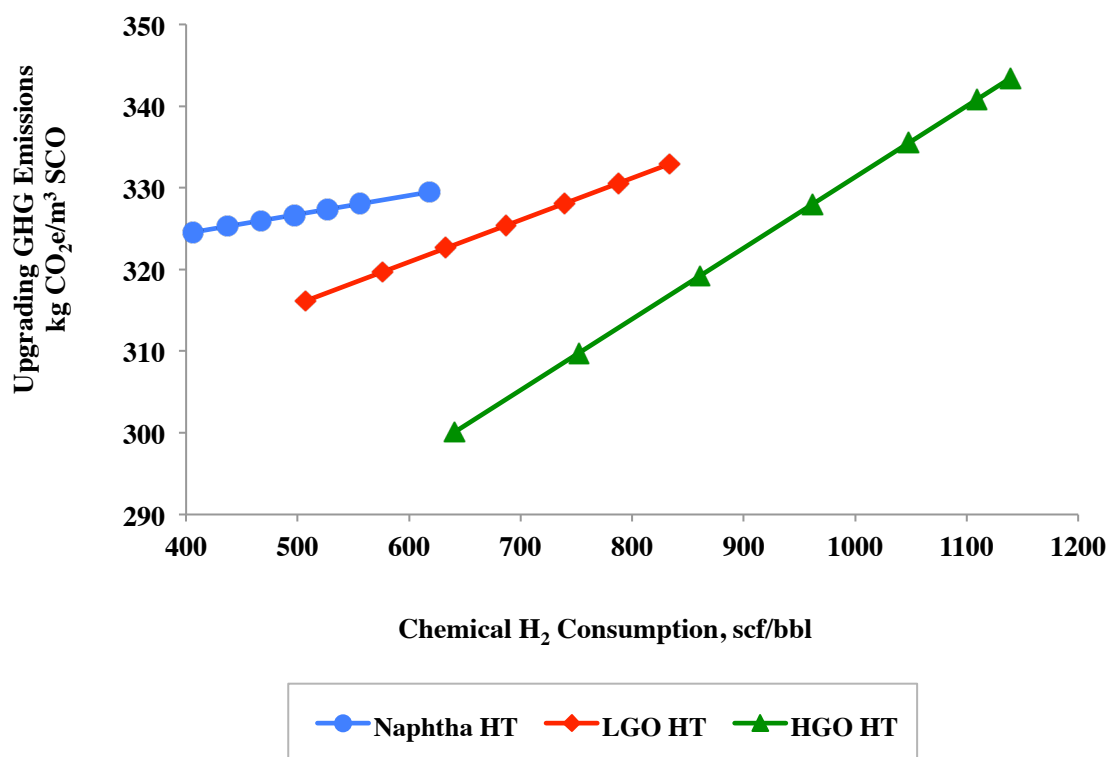


Figure S6. Variation of OSTUM's delayed coking GHG emissions when the chemical hydrogen consumption of the naphtha, LGO, and HGO hydrotreaters is varied.
 Notes: The ranges of chemical hydrogen consumption for each hydrotreater vary in accordance with data in Figure S5. Variations in hydrogen consumption are performed one at the time in OSTUM for the set of conditions defined for the Comparison Scenario. Abbreviations: H₂: hydrogen gas; LGO: light gas oil; HGO: heavy gas oil; HT: hydrotreater.

As previously discussed, the hydrogen consumed in the naphtha hydrotreater has the lowest impact on delayed coking-based upgrading emissions from all hydroprocessing units: a change in hydrogen consumption of 212 scf/bbl can change emissions only by 5 kg CO₂e/m³ SCO (reflected by a gentle slope of 0.02 of the naphtha hydrotreating unit). Delayed coking emissions vary by 17 kg CO₂e/m³ SCO when the hydrogen consumption in the LGO hydrotreater is varied by 327 scf/bbl. Therefore, the rate of change is slightly steeper (slope of 0.05) for this unit indicating a higher influence of hydrogen consumption on emissions. Finally, a variation of 43 kg CO₂e/m³ SCO in delayed coking-

based upgrading emissions is observed in the HGO hydrotreater when its hydrogen consumption varies in a range of 498 scf/bbl (slope of 0.09). The HGO hydrotreater's steepest slope confirms that variations in the hydrogen demand of this unit have the greatest impact on upgrading emissions.

REFERENCES

1. Toman, M.; Curtright, A. E.; Ortiz, D. S.; Darmstadter, J.; Shannon, B. *Unconventional Fossil-Based Fuels: Economic and Environmental Trade-Offs*; RAND Corporation 2008.
2. Serth, R. W., Lestina, T. , Appendix E: Properties of Petroleum Streams. In *Process Heat Transfer: Principles, Applications and Rules of Thumb*, Press, A., Ed. 2014; p P. 599.
3. Perry, M. B., White, C. M. *New Correlations Between the Watson Characterization Factor (Kw) and Properties of Coal-Derived Materials* Division of Coal Science, Pittsburgh Energy Technology Center: Pittsburgh, PA
4. CrudeMonitor, Crudemonitor.ca. Crude Quality Inc.: Edmonton, AB, 2015.
5. Abella, J. P.; Bergerson, J. A., Model to Investigate Energy and Greenhouse Gas Emissions Implications of Refining Petroleum: Impacts of Crude Quality and Refinery Configuration. *Environmental Science & Technology* **2012**, *46*, 13037-13047.
6. ExxonMobil. About Cold Lake Blend.
http://www.exxonmobil.com/crudeoil/about_crudes_cold.aspx (accessed February 18, 2015).
7. Wikipedia. Western Canadian Select.
http://en.wikipedia.org/wiki/Western_Canadian_Select (accessed February 18, 2015).
8. CenovusEnergy. *Christina Lake Dilbit Blend Material Safety Data Sheet*; CenovusEnergy: April 22, 2014, 2014.
9. Yui, S., Chung, K. H. , Processing Oil Sands Bitumen is Syncrude's R&D Focus. *Oil & Gas Journal* **2001**.
10. Parkash, S., *Refining Processes Handbook* Elsevier: Burlington, MA. USA., 2003.
11. Gary, J. H., Handwerk, G. E., *Petroleum Refining, Technology and Economics*. Fourth Edition ed.; Marcel Dekker: New York, USA, 2001.
12. Maples, R. E., *Petroleum Refinery Process Economics*. PennWell Books: Tulsa, Oklahoma, 1993.
13. Meyers, R. A., *Handbook of Petroleum Refining Processes*. 3rd Edition ed.; McGraw-Hill: 2004.
14. Leprince, P., *Petroleum Refining: Conversion Processes*. Editions Technip: Paris, 2001.
15. Gray, M. R., *Upgrading Petroleum Residues and Heavy Oils*. Marcel Dekker, Inc. : 1994.
16. Alvarez-Majmutov, A., Chen, J., Munteanu, M., Simulation of Bitumen Upgrading Processes. . *Petroleum Technology Quarterly* **2013**, *Q2*, 31-35.
17. Alvarez-Majmutov, A., Chen, J., Analyzing the Energy Intensity and Greenhouse Gas Emission of Canadian Oil Sands Crude Upgrading Through Process Modeling and Simulation. *Frontiers in Chemical Science and Engineering* **2014**, *8* (2), 212-218.
18. Yui, S., Removing Diolefins from Coker Naphtha Necessary Before Hydrotreating. *Oil & Gas Journal* **1999**, *97* (36), 64-67.
19. Yui, S., Sanford, E. C., Kinetics of Aromatics Hydrogenation of Bitumen-Derived Gas Oils. *The Canadian Journal of Chemical Engineering* **1991**, *69*, 1087-1095.

20. Spath, P. L., Mann, M. K. *Life Cycle Assessment of Hydrogen Production via Natural Gas Steam Reforming*; US Department of Energy (DOE), National Renewable Energy Laboratory (NREL): Golden, Colorado, February 2001, 2001.
21. Charpentier, A. D., Kofoworola, O., Bergerson, J. A., MacLean, H. L., Life Cycle Greenhouse Gas Emissions of Current Oil Sands Technologies: GHOST Model Development and Illustrative Application. *Environmental Science & Technology* **2011**, 45, 9393-9404.
22. Castañeda, L. C., Muñoz, J. A. D., Ancheyta, J. , Comparison of Approaches to Determine Hydrogen Consumption During Catalytic Hydrotreating of Oil Fractions. *Fuel* **2011**, 90, 3593-3601.
23. Yui, S., Sanford, E. C., Mild Hydrocracking of Bitumen-Derived Coker and Hydrocracker Heavy Gas Oils: Kinetics, Product Yields, and Product Properties. *Industrial & Engineering Chemistry Research* **1989**, 28 (9), 1278-1284.
24. Gray, M. R., *Upgrading Oilsands Bitumen and Heavy Oil*. Pica Pica Press, The University of Alberta Press: Edmonton, Alberta, 2015.
25. Edgar, M. D., Hydrotreating Q&A. In *1993 NPRA Annual Meeting*, San Antonio, TX, 1993.
26. Ancheyta, J., Correlations and Other Aspects of Hydroprocessing. Hydrogen Consumption. In *Modeling of Processes and Reactors for Upgrading of Heavy Petroleum*, CRC Press, Taylor & Francis Group: Boca Raton, FL. , 2013; p 473.
27. Ancheyta, J., Modeling of Catalytic Hydroprocessing. In *Modeling of Processes and Reactors for Upgrading of Heavy Petroleum*, CRC Press, Taylor & Francis Group: Boca Raton, FL, 2013.
28. Villasana Y., L.-L., M. A., Méndez, F. J., Labrador, H., Brito, J. L. , Upgrading and Hydrotreating of Heavy Oils and Residua. *Energy Vol 3: Oil and Natural Gas*.
29. Bose, D. *Design Parameters for a Hydro desulfurization (HDS) Unit for Petroleum Naphtha at 3500 Barrels per Day*; University of Petroleum & Energy Studies, College of Engineering Studies: India, 2015; pp 99-111
30. Volk, M., Wisecarver, K.D., Sheppard, C.M. *Fundamentals of Delayed Coking*; University of Tulsa Tulsa, OK., 2002.
31. Robinson, P. R.; Dolbear, G. E., Hydrotreating and Hydrocracking. In *Practical Advances in Petroleum Processing*, Hsu, C. S.; Robinson, P. R., Eds. Springer New York: 2006; Vol. 1, p 29.
32. *GREET 2013 Life-Cycle Model: User Guide*; Argonne National Laboratory: Lemont, IL October 31, 2013, 2013.
33. Doluweera, G. H., Jordaan, S. M., Moore, M. C., Keith, D. W., Bergerson, J. A. , Evaluating the Role of Cogeneration for Carbon Management in Alberta. *Energy Policy* **2011**, 39, 7963–7974.
34. *GHGenius Model 4.03: Data and Data Sources*; Prepared by (S&T)2 Consultants Inc. for Natural Resources Canada: Ottawa, Ontario, June 15, 2013, 2013.
35. GREET 1 2015 (Fuel-Cycle Model). Laboratory, A. N., Ed. Argonne, IL, 2015.
36. Unitrove Natural Gas Calorific Value Calculator.
<http://www.unitrove.com/engineering/tools/gas/natural-gas-calorific-value> (accessed January 22, 2016).
37. Szklo, A., Schaeffer, R., Fuel Specification, Energy Consumption and CO2 Emission in Oil Refineries. *Energy* **2007**, 32, 1075–1092.

38. Ordorica-Garcia, G.; Croiset, E.; Douglas, P.; Elkamel, A.; Gupta, M., Modeling the Energy Demands and Greenhouse Gas Emissions of the Canadian Oil Sands Industry. *Energy & Fuels* **2007**, *21* (4), 2098-2111.
39. AER ST39: *Alberta Mineable Oil Sands Plant Statistics*; Alberta Energy Regulator: Calgary, Alberta, September 2015, 2015.
40. AER Alberta's Electricity Statistics.
<http://www.energy.alberta.ca/electricity/682.asp> (accessed Jan 21, 2016).
41. Climate Leadership Plan: Coal and electricity. <http://www.alberta.ca/climate-coal-electricity.cfm> (accessed February 9, 2016).
42. Keesom, W., Unnasch, S., Moretta, J. *Life Cycle Assessment Comparison of North American and Imported Crudes*; File No: AERI 1747; Jacobs Consultancy, Life Cycle Associates for Alberta Energy Research Institute: Chicago, Illinois July 2009, 2009.
43. Bohm, M., Brasier, R., Keesom, B., Vogel, C. *A Greenhouse Gas Reduction Roadmap for Oil Sands*; Jacobs Consultancy Inc. for CCEMC and Suncor Energy Inc.: May 2012, 2012.
44. Brandt, A. R., Variability and Uncertainty in Life Cycle Assessment Models for Greenhouse Gas Emissions from Canadian Oil Sands Production. *Environmental Science & Technology* **2011**, *46*, 1253-1261.
45. Nimana, B., Canter, C., Kumar, A., Energy Consumption and Greenhouse Gas Emissions in Upgrading and Refining of Canada's Oil Sands Products. *Energy* **2015**, *83*, 65-79.
46. Elgowainy, A., Han, J., Cai, H., Wang, M., Forman, G. S., DiVita, V. B. , Energy Efficiency and Greenhouse Gas Emission Intensity of Petroleum Products at U.S. Refineries. *Environmental Science & Technology* **2014**, *48*, 7612-7624.
47. Rajyalakshmi, S., Patwardhan, K., Balaramakrishna, P. V. , Optimised Hydrogen Production by Steam Reforming: Part I. *Digital Refining* **2012**, *PTQ Q1 2012*
48. Suncor *Report on Sustainability 2015*; Calgary, Alberta, 2015.
49. Hydrotreating, in Catalysis and Catalysts. In *Chemical Processing Handbook*, McKetta, J. J. J., Ed. CRC Press: 1993; p 216.
50. Banerjee, D. K., *Oil Sands, Heavy Oil & Bitumen, From Recovery to Refinery*. PennWell Corporation: Tulsa, OK, 2012.
51. Danial-Fortain, P., Gauthier, T., Merdrignac, I., Budzinski, H., Reactivity Study of Athabasca Vacuum Residue in Hydroconversion Conditions. *Catalysis Today* **2010**, *150*, 255-263.