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Biomass Direct Liquefaction Options: TechnoEconomic and Life Cycle Assessment

PNNL	VTT	Zeton
IJ Tews	K Onarheim	Dave Beckman
Y Zhu	Y Solantausta	
CV Drennan		
DC Elliott		
LJ Snowden-Swan		

July 2014

Pacific Northwest
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Pacific Northwest National Laboratory
Richland, Washington 99352

Contents

Glossary of Terms

Fast pyrolysis – thermal conversion in the absence of oxygen at short residence time, for woody biomass typical conditions are <2 seconds at ~500 °C

Hydrothermal – processing in hot pressurized water

Bio-oil – liquid product of fast pyrolysis

Biocrude – liquid oil product from hydrothermal liquefaction

Upgrading – multi-step hydroprocessing to convert bio-oil in liquid hydrocarbon products

Hydrotreating – single-step hydroprocessing to convert biocrude into liquid hydrocarbon products

Hydroprocessing – chemical reaction with hydrogen gas, typically a catalytic process operated at elevated pressure, usually to remove heteroatoms, remove unsaturation, and reduce molecular weight.

Heavy hydrocarbon -- hydrocarbon product distilling at temperatures higher than diesel

Nth plant – commercial plant operating an established process, not a pioneer plant

1.0 Introduction

The purpose of this work was to assess the competitiveness of two biomass to transportation fuel processing routes, which were under development in Finland, the U.S. and elsewhere. Concepts included fast pyrolysis (FP), and hydrothermal liquefaction (HTL), both are followed by hydrodeoxygenation, and final product refining.

This work was carried out as a collaboration between VTT (Finland), and PNNL (USA). The public funding agents for the work were Tekes in Finland and the Bioenergy Technologies Office of the U.S. Department of Energy. The effort was proposed as an update of the earlier comparative technoeconomic assessment performed by the IEA Bioenergy Direct Biomass Liquefaction Task in the 1980s. [1] New developments in HTL and the upgrading of the HTL biocrude product triggered the interest in reinvestigating this comparison of these biomass liquefaction processes. In addition, developments in FP bio-oil upgrading had provided additional definition of this process option, which could provide an interesting comparison.

Concepts employing syngas or biological processing to transportation fuels were excluded. It was not within the scope of this project to analyze a large number of alternatives in detail. The reader is referred, as an alternative, to a recent study[2], where several alternative technologies were compared. A summary of that study is presented in Figure 1 below. The study suggested that fast pyrolysis to transportation fuels may be a viable alternative in the future, especially so if integration to a petroleum refinery was employed. The study also emphasized the fact that cost estimates of products for pioneer plants are significantly greater than for the nth plants.

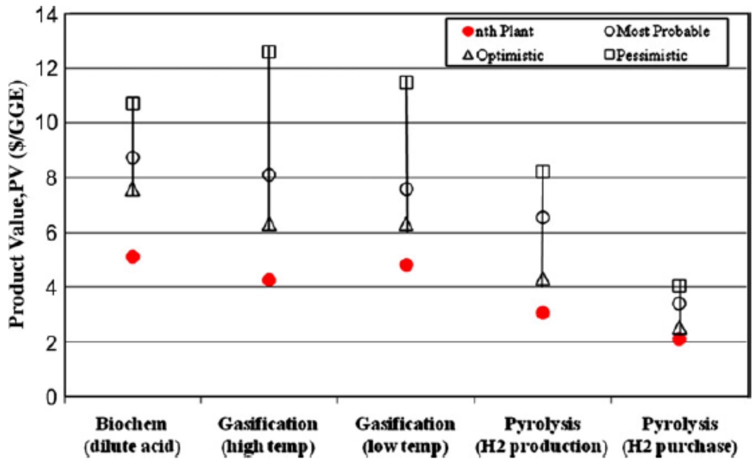

Figure 1. Estimates of product values for biofuel technologies by Anex et al.[2]

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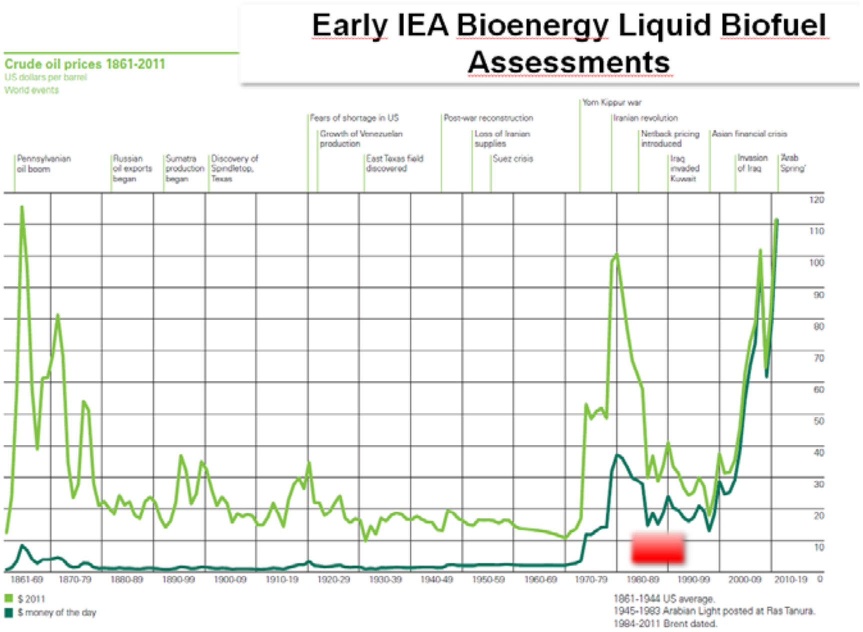
[1] Beckman, D., et al. Techno-Economic Assessment of Selected Biomass Liquefaction Processes. Final Report of IEA Cooperative Project Direct Biomass Liquefaction. VTT Research Reports 697 Technical Research Centre of Finland, Espoo **1990**.

[2] Anex, R. et al. *Techno-economic comparison of biomass-to-transportation fuels via pyrolysis, gasification, and biochemical pathways*. Fuel **2010** 89:29–35.

The work reported by Anex et al. included analysis of published process data on the subject technologies, evaluation of reliability of data, generation of complete process concepts, building Aspen Plus® performance balance models for these concepts, and estimating industrial scale performance balances as bases for sizing of equipment, and estimating investment and operational costs. Various sensitivity studies were carried out to define preferred concepts and their critical parameters. Missing data was reported, and further work on generating missing data of most promising concepts was suggested. Special emphasis was placed in evaluating the uncertainty related to comparison of processes under different stages of development. It poses special challenges in evaluating costs for these systems.

1.1 Prior Related Work

After the first oil price crisis, an effort was made to establish a synthetic fuel industry in the U.S. using coal and more unconventional fossil fuel sources. Later in the 1970's, biofuels were also introduced and developed. For example, the IEA Bioenergy established a series of projects where the development potential of new biomass liquefaction process concepts under development in participating countries (U.S., Canada, Sweden, Finland) was evaluated[3]. Duration of these studies is illustrated in Figure 2, which also explains why there was little industrial interest towards these systems. The early IEA assessments were carried out from 1982-92 during which oil prices plummeted to one third from the peak level.



http://www.bp.com/assets/bp_internet/globalbp/globalbp_uk_english/

Figure 2. Price of oil 1860-2011, light green line in 2011 dollars.
(red bar denotes duration of the IEA projects)

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[3] *A Study of a Biomass Liquefaction Test Facility, Final Report of IEA Cooperative Project Biomass Liquefaction Test Facility*, Kjellström, B. ed. **1985** Statens Energiverk R:1, Stockholm.

Evaluation of alternative transportation fuel production processes at that time was just beginning. Complete experimental mass balances were not available, and the studied process routes to transportation fuels were somewhat premature. A comparison of high-pressure biomass liquefaction (i.e. hydrothermal liquefaction) and fast pyrolysis to transportation fuels is summarized in Figure 3 below. Costs related to three stages of processing (primary conversion, oil upgrading, and final refining) are shown. Efficiencies for the "potential" concepts for fast pyrolysis and high pressure liquefaction processes to transportation fuels were 50 and 39 % based on fuel LHV, respectively.

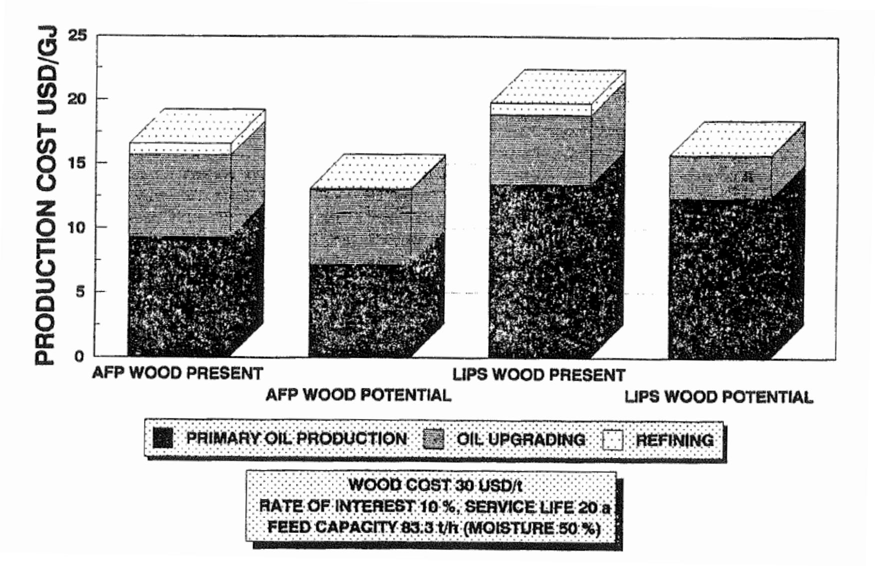

Figure 3. Production cost comparison of transportation fuels from biomass, costs for 1987[4].

Fast pyrolysis was selected in these three consecutive IEA assessments[4],[1],[5] as the potentially most promising technology among the numerous biomass liquefaction routes for the production of fuel oils and transportation fuels, which were under development at the time of assessment.

First-of-a-kind synthetic fuel plants produced much higher cost fuels than initially estimated around 1975-80. Merrow et al.[6,7] analyzed and pointed out a few fundamental mistakes, which plagued early industrial efforts. They established a cost evaluation method, which tried to capture the main negative drivers. Ultimately however, interest towards synfuels was reduced considerably with decreasing oil prices (note Fig 2), and there was relatively limited development during the 1990's. This is strong reminder that development efforts for alternative fuels are directly linked to the price of crude oil.

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[4] McKeough, P. et al. *Techno-ecomonic assessment of direct biomass liquefaction processes. Final Report of IEA Cooperative Project Biomass Liquefaction Test Facility*. VTT Research Report 337, Technical Research Centre of Finland, Espoo. **1985**.

[5] Solantausta, Y. et al. *Assessment of liquefaction and pyrolysis systems.* Biomass Bioenergy, **1992** 2(1-6):279-297.

[6] Merrow, E., Chapel, S., Worthing, C., *A review of cost estimation in new technologies: Implications for energy process plants*. RAND-R-2481-DOE. RAND Corporation for the U.S. Department of Energy. Santa Monica, CA. July **1979**.

[7] Merrow, E., Phillips, K., Myers, C., *Understanding cost growth and performance shortfalls in pioneer process plants*. R-2569-DOE, RAND Corporation for the U.S. Department of Energy. Santa Monica, CA.. September **1981**.

Once oil prices started to rise again in the early 2000s, sustainable renewable biofuels became the next synthetic fuels of interest. Reduction of the carbon footprint had become an issue, and biofuels offered a potential solution.

Holmgren et al.[8] re-introduced fast pyrolysis and bio-oil hydrotreating to mainstream engineering discussion as a potential route to alternative renewable, liquid transportation fuels in 2008. Fast pyrolysis could serve transportation fuels markets using feedstock outside the food chain. As a result of this article, industry interest in biomass pyrolysis-derived fuels was awakened because the article was co-authored by both industrial and national laboratory stakeholders, UOP, PNNL and NREL. It was recognized that before industrial applications could be achieved, the new route to fuels would require considerable development efforts. However, it was reported that the route had industrial potential to be cost competitive with currently elevated petroleum product prices, along with CO_2-reduction potential.

The U.S. DOE BETO published in 2009 a document, *Production of Gasoline and Diesel from Biomass via Fast Pyrolysis, Hydrotreating, and Hydrocracking, a design case*.[9] Based on the analysis, 29 wt% of renewable gasoline and diesel blendstock could be produced from wood feedstock at 7wt% moisture. Additionally, fossil hydrogen was assumed for hydrotreating. PNNL and NREL prepared this report, which detailed cost and performance analysis on infrastructure-ready products from the production and upgrading of pyrolysis oil to hydrocarbon fuels. They also concluded that the route would be an economically attractive source of renewable fuels. They reported 55 % of the feedstock carbon reported to products (gasoline and diesel pool). However, it was also reported that in their model 12 % of feed carbon was derived from natural gas (NG), which was used to generate hydrogen for bio-oil hydrotreatment. For this reason, the report emphasised that integration of biomass upgrading with a petroleum refinery would improve the economic performance of the concept.

The report of Wright et al.[10] by Iowa State University, Conoco, and NREL was the first study to employ the pioneer plant method for estimating investment cost contingencies in reporting biofuel cost estimates. An investment plant cost in excess of $900 million was calculated for a demonstration plant using 2000 t/d biomass feed employing first-of-a-kind investment cost bases. The nth plant cost would be one third of that. When hydrogen for upgrading is generated from biomass, a biomass to liquid fuel efficiency for the hydrogen production scenario was estimated at 36%. Feedstock to liquid fuel energy conversion efficiency for the hydrogen purchase scenario is estimated at 50% and includes the hydrogen energy input. The authors list several technical challenges, which still must be overcome to make the concept industrially viable. These include the challenges of alkaline content of biomass which can impact catalytic treatment and improvements in condenser technology at the scale employed to improve yield of liquid bio-oil and reduce material build-up in the system. Bio-oil upgrading faces several major challenges including: catalyst performance and lifetime, uncertainty over bio-oil separation technology performance, and the need for multiple process steps for hydrotreating.

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[8] Holmgren, J. et al. *Consider upgrading pyrolysis oils into renewable fuels.* Hydrocarbon Processing **2008**(Sep): 95-103

[9] Jones, S.B.et al. *Production of gasoline and diesel from biomass via fast pyrolysis, hydrotreating and hydrocracking: a design case.* PNNL-18284, Pacific Northwest National Laboratory, Richland, Washington February **2009**.

[10] Wright, M. et al. *Techno-economic analysis of biomass fast pyrolysis to transportation fuels*. Fuel **2010** 89:S2–S10

The processing scheme consisting of a forestry residue biomass fast pyrolysis followed by hydrodeoxygenation by co-feeding a mineral-oil refinery was proposed and evaluated in the EU project BIOCOUP.[11] The results of these several studies and some related versions are collected in Figure 4 below. The transportation pool component (gasoline + light oil) efficiency for the concept, where vacuum gas oil and bio-oil, upgraded by HDO, were co-processed in a FCC, was estimated to be 43 % when considering the LHV of the biomass fed to pyrolysis and fossil hydrogen used in bio-oil upgrading. In this case, HDO340 means incomplete bio-oil HDO carried out at 340 °C. The pioneer plant method was employed in estimating capital costs. Demonstration plant production costs were estimated to be 2.3 times more expensive than the estimated costs for the nth plant for the HDO340 case.

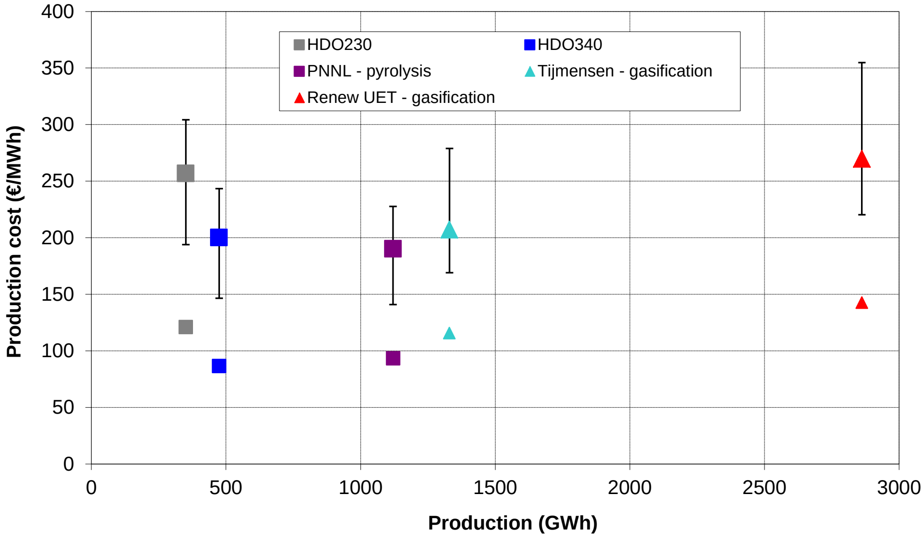

Figure 4. Gasoline production cost estimates from biofuels, HDO230 and HDO340 concepts from BIOCOUP co-refining, PNNL[9], Renew[12], Timensen[13]. Ranges refer to the range pioneer plant method intervals.

1.2 Current Study

Building upon all of the prior related work, this current study intends to perform a modern assessment of fast pyrolysis (FP) and hydrothermal liquefaction (HTL) both followed by hydrodeoxygenation to produce a liquid hydrocarbon product, defined in terms of a gasoline, diesel and heavy oil compatible fractions. Forest residue wood biomass was the feedstock used in the model. The concepts were selected due to the similar development challenges with these concepts and similar stage of development.

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[11] http://www.biocoup.com/index.php?id=18

[12] RENEW - Renewable fuels for advanced powertrains, 2008, http://www.renew-fuel.com/home.php.

[13] Tijmensen, M.J.A., et al. *Exploration of the possibilities for production of Fischer Tropsch liquids and power via biomass gasification*, Biomass Bioenergy **2002** 23:129-152.

This current evaluation was an extension of the assessment carried out within the IEA Bioenergy agreement during the 1980's. A fresh assessment was needed, using recent research data and process improvements to inform a techno-economic evaluation that could guide the efforts of stakeholders interested in developing these systems and identify high value topics for national research investments in bringing the technology to fruition. This has resulted in a higher confidence assessment due to the recent abundance of experimental research data and industrial activities available than during prior evaluations.

Fast pyrolysis of biomass to replace fuel oils was recently scaled-up to industrial operation by Valmet, Ensyn and BTG. Examples of industrial projects for heat or power production are those of Fortum Power and Heat[14] in Finland, BTG BTL[15] in the Netherlands, Green Fuel Nordic Oy[16] in Finland, and Ensyn's expansion in Canada and an announced project with Premium One in Malyasia.[17] There has also been the first industrial pilot plant for the production of transportation fuels through fast pyrolysis and hydrotreatment by UOP[18] under construction in Hawaii, supported in-part by the U.S. DOE and was expected to be fully operational in 2015. Therefore, industrial applications producing higher value fuels may be expected prior 2020.

The impetus for this study was to determine if recent advancements in both fast pyrolysis bio-oil upgrading and in hydrothermal liquefaction may have impacted the relative cost competitiveness of these two routes. For example, it has been found that the hydrotreating of fast pyrolysis bio-oil modeled in the earlier report[1] will need additional processing for stabilization of the bio-oil, so a reduced space velocity is required. Also, the reducing gas requirement in the earlier report for HTL (and therefore a need for significant diversion of biomass feedstock to the gasification process) was not needed. In addition, the once through HTL process without biocrude recycle for slurry formation has now been demonstrated. These important developments are modeled in this study.

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[14] http://www.fortum.com/en/mediaroom/Pages/fortum-invests-eur-20-million-to-build-the-worlds-first-industrial-scale-integrated-bio-oil-plant.aspx

[15] http://www.empyroproject.eu/

[16] http://www.greenfuelnordic.fi/en/page/23?newsitem=10

[17] http://www.ensyn.com/projects/renfrew-ontario/ http://www.ensyn.com/projects/indi-projectitaly/ http://www.ensyn.com/projects/lahad-datumalaysia/ http://www.industriaeinnovazione.it/en/ER-sito-Indi.pdf page 37

[18] http://www.uop.com/honeywells-uop-awarded-department-energy-grant-conversion-waste-biomass-green-transportation-fuels/

2.0 Analysis Approach

A techno-economic assessment is a standard tool for evaluating alternatives. The accuracy of this tool is highly dependent on the quality and reliability of the data at hand, thus the techno-economic viability of undemonstrated process concepts can be difficult to evaluate.

Conceptual models of the conversion processes fast pyrolysis and hydrothermal liquefaction of biomass with upgrading of bio-oil have been developed using process simulation software Aspen Plus®. The models are based on literature data and experimental results from partners involved in the project. Inherent differences in the process equipment and products were captured in this assessment. Fast pyrolysis bio-oil is a more thermally unstable feedstock for catalytic hydroprocessing than petroleum-derived feedstocks and therefore requires a more nuanced approach in upgrading. Hydrothermal liquefaction produces a more stable biocrude for upgrading, at the expense of high-pressure processing equipment and lower product yield, but can be more easily hydrotreated to the hydrocarbon liquid fuel products desired in this study with lower processing cost impact.

Aspen Plus® simulates steady-state chemical process reactions and calculates mass and energy balances based on experimentally derived operating conditions. Furthermore, physical properties of the chemical compounds chosen to represent the reactants and products were provided by the Aspen Plus® thermodynamic database. Heat and material balances generated by the models were further validated and then used to complete a technoeconomic assessment (TEA).

In order to model the biomass liquefaction technologies, model compound mixtures needed to be defined to represent the products of both the liquefaction step but also the hydroprocessing product. The organic products are a complex mixture of hundreds of compounds. The number and type of compounds used in the Aspen model to represent the organic liquid products and the associated aqueous phase must reasonably match key properties of such as C, H, O, N, S, density, heating value, GC/MS data, distillation range, and aqueous solubility. A significant effort and time was spent on development and refining of these lists. Based on earlier models at PNNL and VTT, an updated list of model compounds was developed for fast pyrolysis bio-oil. Using that list as a starting point a second list was developed for hydrothermal liquefaction. Whereas the hydroprocessed products from the two liquefaction technologies are nearly the same, the model compound list developed to represent the hydrocarbon liquid fuel product was the same for each liquefaction model.

A model compound list for fast pyrolysis bio-oil was developed as shown in **Table 1**. These are for the most part commonly found components in bio-oil. However, each component also represents a group of similar components in real bio-oil. A user defined component, pyrolignin was created to allow for a better representation of bio-oil in ASPEN since there is no lignin oligomer component in the Aspen data base.

HTL organic products are a complex mixture of hundreds of compounds. The compounds chosen for the Aspen model are shown in **Table 2.** Note, that this list does not imply that these compounds occur in the given percentages in actual HTL biocrude, rather each compound represents a group of compounds that taken together exhibit the bulk properties. Carbon dioxide and ammonia in the aqueous phase actually form their ionic species in various amounts and types, including NH_4^+, NH_2COO^-, HCO_3^-, $CO_3^=$. For simplification purpose, these ion formations are not simulated in this model, but their pure original compounds are considered.

Table 1. Compounds Used to Model Fast Pyrolysis Bio-oil

HTL OIL	Wt%	C	H	O	N	S	CAS
Acetic Acid	2.7%	2	4	2			64-19-7
Ethylene glycol	0.1%	2	6	2			107-21-1
Acetol	2.9%	3	6	2			116-09-6
Glycolaldehyde	8.7%	2	4	2			141-46-8
Guaiacol	11.4%	7	8	2			90-05-1
Furfural	2.7%	5	4	2			98-01-1
Levoglucosan	27.5%	6	10	5			498-07-7
Water	28.7%	0	2	1			7732-18-5
Oleic Acid	8.5%	18	34	2			112-80-1
ethylthioethanol	0.1%	4	10	1		1	110-77-0
2-Pyrrolidone	2.0%	4	7	1	1		616-45-5
Pyrolignin	4.7%	24	32	4			User Defined
Total	**100%**						

Table 2. Compounds Used to Model HTL Gas and Liquid Products

HTL OIL	Wt%	C	H	O	N	S	CAS
2-Pyrrolidone	0.12%	4	7	1	1		616-45-5
ethylthioethanol	0.01%	4	10	1		1	110-77-0
2-Butanone	1.62%	4	8	1			78-93-3
1,2-Benzenediol	0.00%	6	6	2			120-80-9
4-propyl-1,3-Benzenediol	7.75%	9	12	2			18979-60-7
dihydro-5-methyl-2(3H)-Furanone	0.03%	5	8	2			108-29-2
2,6-dimethoxy-Phenol	2.70%	8	10	3			91-10-1
4,5-dimethyl-1,3-Benzenediol	8.11%	8	10	2			527-55-9
2-methoxy-4-propyl-Phenol	24.38%	10	14	2			2785-87-7
Cyclopentanone	5.41%	5	8	1			120-92-3
2-methyl-Cyclopentanone	3.25%	6	10	1			1120-72-5
2-methyl-2-Cyclopenten-1-one	0.41%	6	8	1			1120-73-6
Phenol	1.64%	6	6	1			108-95-2
2,3-dimethyl-2-Cyclopenten-1-one	2.57%	7	10	1			1121-05-7
4-methyl-Phenol	2.27%	7	8	1			106-44-5
Diphenylmethane	7.30%	13	12				101-81-5
Benzyl ether	9.74%	14	14	1			103-50-4
9-methylanthracene	14.62%	15	12				779-02-2
Pyrolignin	1.08%	24	32	4			User Defined
Formic Acid	1.46%	1	2	2			64-18-6
Water	5.53%		2	1			7732-18-5
Total	**100%**						

The hydroprocessed products from the biomass liquefaction systems contain numerous compounds and a limited number is used for modeling purposes. **Table 3** shows the mixture of compounds used to represent the hydrotreated oil in the models. Note, that this list does not imply that these compounds occur in the given percentages in actual hydrotreated oil, rather each compound represents a group of compounds that taken together exhibit the bulk properties.

Table 3. Compounds Used to Model Hydroprocessed Products

Compound	**C**	**H**	**O**	**N**	**S**	**Wt%**	**CAS**
Hexane	6	14				3.7%	110-54-3
Dodecane	12	26				4.4%	112-40-3
4-methylnonane	10	22				4.1%	17301-94-9
ethylcyclopentane	7	14				2.9%	1640-89-7
1-methyl-1-ethylcyclopentane	8	16				3.7%	16747-50-5
Cyclohexane	6	12				3.2%	110-82-7
propylcylcohexane,	9	18				3.2%	1678-92-8
1,3-dimethyladamantane	12	20				4.7%	702-79-4
1-ethenyl-4-ethyl-Benzene	10	12				7.0%	3454-07-7
4-methylphenanthrene	15	12				24.4%	832-64-4
Indeno[1,2,3-cd]pyrene	22	12				6.8%	User Defined
1,2-Diphenylethane	14	14				8.3%	103-29-7
Indane	9	10				3.4%	496-11-7
1-n-hexyl-1,2,3,4-tetrahydronaphthalene	16	24				17.1%	66325-11-9
1-phenyl-Naphthalene	16	12				2.9%	605-02-7
5-Methyl-2-(1-methylethyl)phenol	10	14	1			3.7%	89-83-8
2-4-6-Trimethyl-pyridine	8	10		1		4.4%	108-75-8
Dibenzothiophene	12	5			1	4.1%	132-65-0
Total						**100%**	

Numerous technical assumptions were made in order to accomplish this modeling task due to the early stage of development of these biomass conversion technologies. Feedstock analyses used in the models are based on extensive research conducted on biomass material at VTT. Chipped forest residue was assumed as raw material for the bio-oil production processes. **Table 4** shows the specification of the feedstock as a summary. Moisture content of the received biomass feedstock is assumed to be at 50%.

Table 4. Summary of Feedstock Properties Based on Dry Matter.

Proximate Analysis, %		Ultimate Analysis, %	
Ash	1.5	Ash	1.5
FC	18.5	C	50.9
VM	80.0	H	6.0
		N	0.3
		S	0.03
		O	41.3

Because fast pyrolysis (FP) and hydrothermal liquefaction (HTL) conversion processes require different types of feedstock preparation, the method of preparation and feeding to the reactor will be discussed in subsequent chapters. The same feedstock was used consistently in all model development and analysis. Pre-treatment (grinding and drying) is done at the plant. Size reduction and particle drying for fast pyrolysis is well understood. In the case of hydrothermal liquefaction there is less information and an assumed low concentration of biomass in water was assumed as a conservative basis. The use of recycle water for heat transfer to the feedstock is an untested method which was assumed for this analysis.

The plant capacity is set at processing a total of 2000 metric tons per day (474 MW) of bone-dry biomass (x MW), in order that the studies will be on a basis similar to that which was used by the Bioenergy Technologies Office of U.S. Department of Energy.[9] In the model, the 2000 metric tons per day are processed through four 500 mtpd reactor units for FP, instead of one large unit. The reactor size was based on literature reports on reactor size for fast pyrolysis. HTL processing is in an earlier stage of development and therefore the assumed reactor train size (2000 metric ton per day) may be more open to question. The plant is assumed to be an established ("nth") plant design rather than a first of its kind (pioneer) plant.

The upgrading of the liquefaction products is also at an early stage of development. The 3 stage hydrotreating model used here for fast pyrolysis bio-oil has been demonstrated for extended periods in the laboratory, but has not been scaled up. The exothermic nature was not adequately modeled here so that the full impact is not incorporated. A single stage of hydrotreating for the HTL biocrude has also been tested in the laboratory but there is no long term validation of the method available from which to extrapolate catalyst lifetime.

The production of hydrogen from the product gases has not been tested for these specific cases. In addition, the assumed use of the hydrotreater byproduct water and the condenser blow down for makeup water in the steam reformer are also untested.

Finally, the long-term catalyst lifetimes assumed here have not been demonstrated for either the bio-oil hydroprocessing or for the steam reforming.

3.0 Process Design for Biomass Conversion to Liquids

Two energy conversion routes were considered:

1. Fast pyrolysis of biomass and upgrading of the bio-oil product,
2. Hydrothermal liquefaction of biomass and hydrotreating of the biocrude product.

In both cases the desired end product was the same: a mixture of liquid hydrocarbon that boil in the ranges of gasoline, diesel and heavy fuel oils. Based on experimental data, Aspen Plus® models were generated for each of the biomass liquefaction choices, fast pyrolysis with bio-oil upgrading and hydrothermal liquefaction with biocrude hydrotreating.

3.1 Fast Pyrolysis and Upgrading

The fast pyrolysis and upgrading process includes raw material preprocessing, pyrolysis and upgrading with separation into gasoline, diesel, and heavy hydrocarbon boiling range fractions -- all on a single site. Heat input to the fast pyrolysis process is generated in the char-fired boiler. **Figure 5** shows the block diagram for the process. Modelling the pyrolysis reactor with yields has been based on a compilation of experimental results[19] and the model for the upgrading was based on experimental results, as well.[20]

3.1.1 Biomass Pretreatment

The first step in biomass pretreatment for the fast pyrolysis process is drying the feedstock from 50 wt% moisture as received to about 8-10 wt% moisture. This is done in a conventional belt dryer that can use a variety of energy sources, for instance, steam, hot water and electricity. Heat for the modeled dryer is generated in the char-fired boiler as steam and hot water. After drying, the biomass is ground to particle size < 5 mm.

Raw material moisture strongly affects the product bio-oil moisture. The higher the bio-oil moisture, the lower is its heating value. As a consequence, raw material for the fast pyrolysis process must be dried to approximately 8-10 wt% moisture in order to keep the bio-oil moisture below 30 wt%, at which point phase separation occurs. The use of dried biomass also facilitates the fast heat-up in the pyrolysis process required for high bio-oil yield. The forest residue is also ground to a particle size of below 5 mm. The small size is necessary in order to ensure complete reaction of the particle during the short residence time in the reactor.

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[19] Oasmaa, A. et al. *Fast pyrolysis bio-oils from wood and agricultural residues*. Energy Fuels, **2009** 24:1380-1388. doi: 10.1021/ef901107f

[20] Elliott, D.C. et al. *Catalytic hydroprocessing of fast pyrolysis bio-oil from pine sawdust.* Energy Fuels, **2012** 26:3891-3896. doi: 10.1021/ef3004587

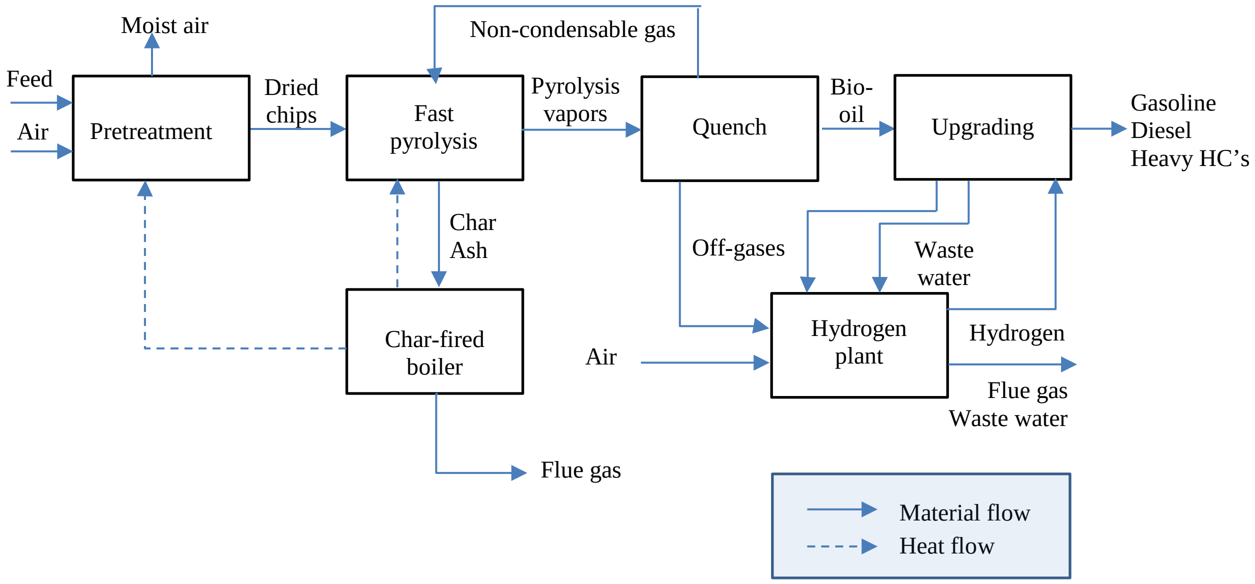

Figure 5. Fast pyrolysis and bio-oil upgrading process flow diagram

3.1.2 Fast pyrolysis

Ground, dried biomass enters a circulating fluidized bed reactor and is rapidly heated to 520°C under atmospheric pressure in an oxygen-free environment. The reactor is heated with hot sand from the char boiler. After a biomass particle residence time of 1–2 seconds the resulting pyrolysis vapors, non-condensable gases, char and sand exit the reactor. Char and sand are separated directly after the reactor in cyclones and sent to the char boiler where char is combusted and sand is re-heated. Pyrolysis vapors and non-condensable gases are sent to a quench tower. Vapors are quickly condensed to about 35°C in order to limit the rate of secondary and polymerization reactions in the bio-oil product. Condensed bio-oil is used as quenching medium in the quench tower. Non-condensable gases exit the quench tower in gas phase. Part of these gases are recycled to the reactor as fluidizing medium. The rest of the gases are used as fuel in the hydrogen reformer. **Figure 6** shows the fast pyrolysis process that was modeled.

The products from fast pyrolysis are detailed in **Tables 5-7.**

Table 5. Fast Pyrolysis Yield, wt% Based on Dry Biomass Feedstock

Products	mass	carbon basis
Bio-oil	51.2	54.9
Char	24.4	35.7
Reaction Water	12.3	0
Gas	12.1	9.4

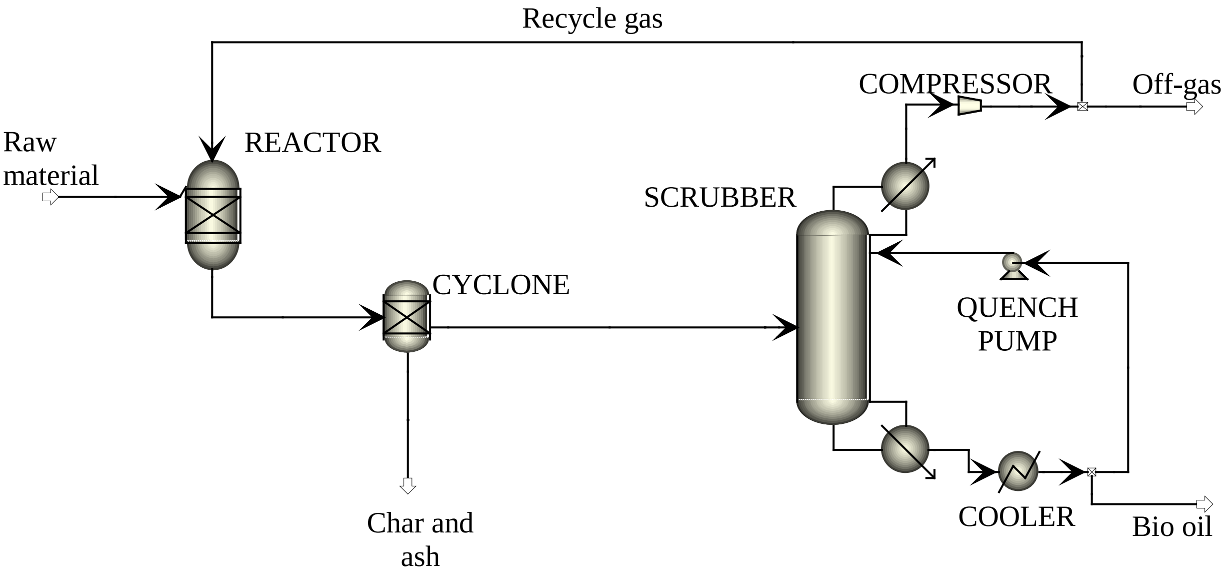

Figure 6 Unit Operations in the Fast Pyrolysis Plant

Table 6. Bio-oil Composition

Bio-oil Components	wt%
Organic phase	71.3
Water	28.7

Table 7. Gas Phase Composition

Gas Component	mole %
CO_2	32.5
CO	43.0
CH_4	12.0
H_2O	6.4
Ethylene	4.7
Ethane	1.4

Bio-oil produced in the fast pyrolysis process is unstable and cannot be directly blended with conventional fossil fuels. The bio-oil is put through a hydrotreatment process where hydrogen is used to upgrade the unstable oil by de-oxygenation. The upgraded bio-oil is then distilled into hydrocarbon fractions that boil in the gasoline, diesel, and heavy ranges.

3.2 Hydrothermal Liquefaction and Hydrotreating

Hydrothermal liquefaction (HTL) and subsequent hydrotreating (see **Figure 7**) is defined by five major processing areas: feedstock pretreatment, HTL, hydrotreating, hydrogen production and wastewater treatment (and other utilities).

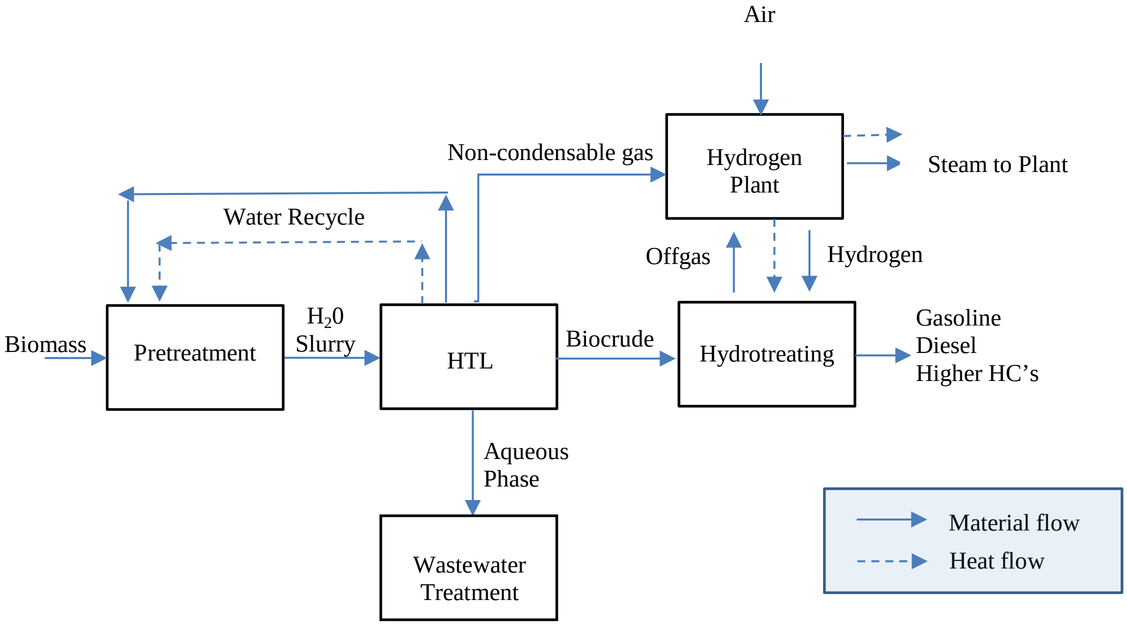

Figure 7. Hydrothermal liquefaction and hydrotreating process flow diagram

In the feedstock pretreatment, forest residue biomass is ground to fine particles without drying and softened by direct injection of hot water, to produce a slurry comprising water with 8 wt% solids loading. It is believed that the particle size for HTL does not need to be reduced to as great degree as in fast pyrolysis, so the difference in grinding costs for the dry chips versus the wet chips has not been accounted for in this study. The slurry is further preheated and pressurized to HTL reaction pressures. Feedstock solids loading specification for the HTL process is based on experimental data from laboratory testing. The base case model, shown in **Figure 8** assumes 8 wt% solids loading in the slurry pumped to about 0.6 MPa and sent to the HTL process area.

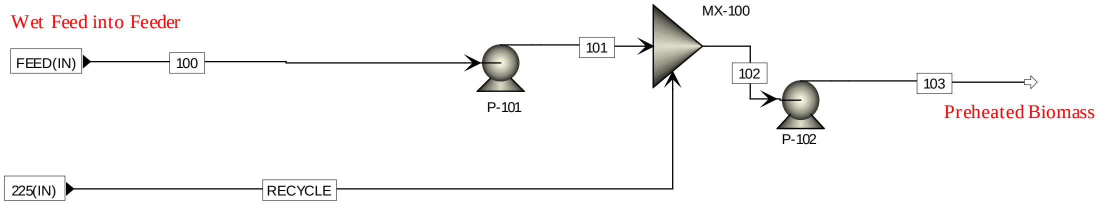

Figure 8. Biomass pretreatment process

The HTL process model is based on experimental tests conducted at PNNL for the National Advanced Biofuels Consortium (NABC).[21] In the process model, the biomass-water slurry from the biomass pretreatment process is assumed to be pumped and preheated by the hot liquid effluent from the HTL reactor. Ongoing work with pump manufacturers indicates that large scale biomass/water slurry pumping is considered feasible; however, this still needs to be verified in field tests.

As seen in **Figure 9**, the preheated slurry is sent to the HTL reactor operating at 20.3 MPa and 355°C. For this large-scale system and the economy of scale-up, the HTL reactor scheme is assumed to be plug flow rather than the CSTR more commonly seen in laboratory experiments. The reactor has a shell and tube design with slurry in the tube and a heat transfer fluid system on the shell side. A heater fired by process gases is used to provide heat to the heat transfer fluid and maintain isothermal conditions in the HTL reactor.

The biomass slurry undergoes a conversion reaction to biocrude, aqueous, and gas phase products. The hot effluent from the HTL reactor is sent to a settler/filter to separate fine particles from the hot liquid. The filtered solids are mainly composed of precipitated minerals with some unreacted biomass or char. Further processing of the separated solids is not considered in this model and the materials are assumed to be disposed as solid wastes. The liquid effluent from the settler/filter exchanges heat with the incoming biomass-water slurry and is then depressurized. After cooling to 117 °C and depressurization to 0.1 MPa the products go through a 3-phase separator, SP-210, and exit in the gas phase, aqueous phase and biocrude product streams S208, S209, and S213 respectively. Yields for each product stream are reported in **Table 8** on both a mass basis and on a carbon basis. All product distribution data from the Aspen mass balance was checked against experimental results produced by PNNL.

Table 8. Hydrothermal Liquefaction Yield, wt% Based on Dry Biomass Feedstock

Products	mass	carbon basis
Organic portion of Biocrude	34.6	52.4
Organics in Aqueous Phase	35.4	36.3
Solids	5.7	0.5
Reaction Water	6.8	-0-
Gas	17.5	10.8

Table 8 indicates a large fraction of biomass converted to organics present in the biocrude phase as well as in the aqueous phase. This amount of organic in the aqueous phase is greatly diluted by the large fraction of water used in the hydrothermal system. The data in **Table 8** represent a single pass yield from the dry biomass solids and do not include the large amount of process water recycled within HTL, in order to reduce the solids loading of the slurry stream to 8 wt%**.**

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[21] Schmidt, A.J. et al. Mid-stage 2 report on the hydrothermal liquefaction strategy for the NABC leadership team. PNNL-21768, Pacific Northwest National Laboratory, Richland, Washington, September **2012.**
Zhu, Y. et al. *Techno-economic analysis of liquid fuel production from woody biomass via hydrothermal liquefaction (HTL) and upgrading.* Applied Energy, in press. **2014**.

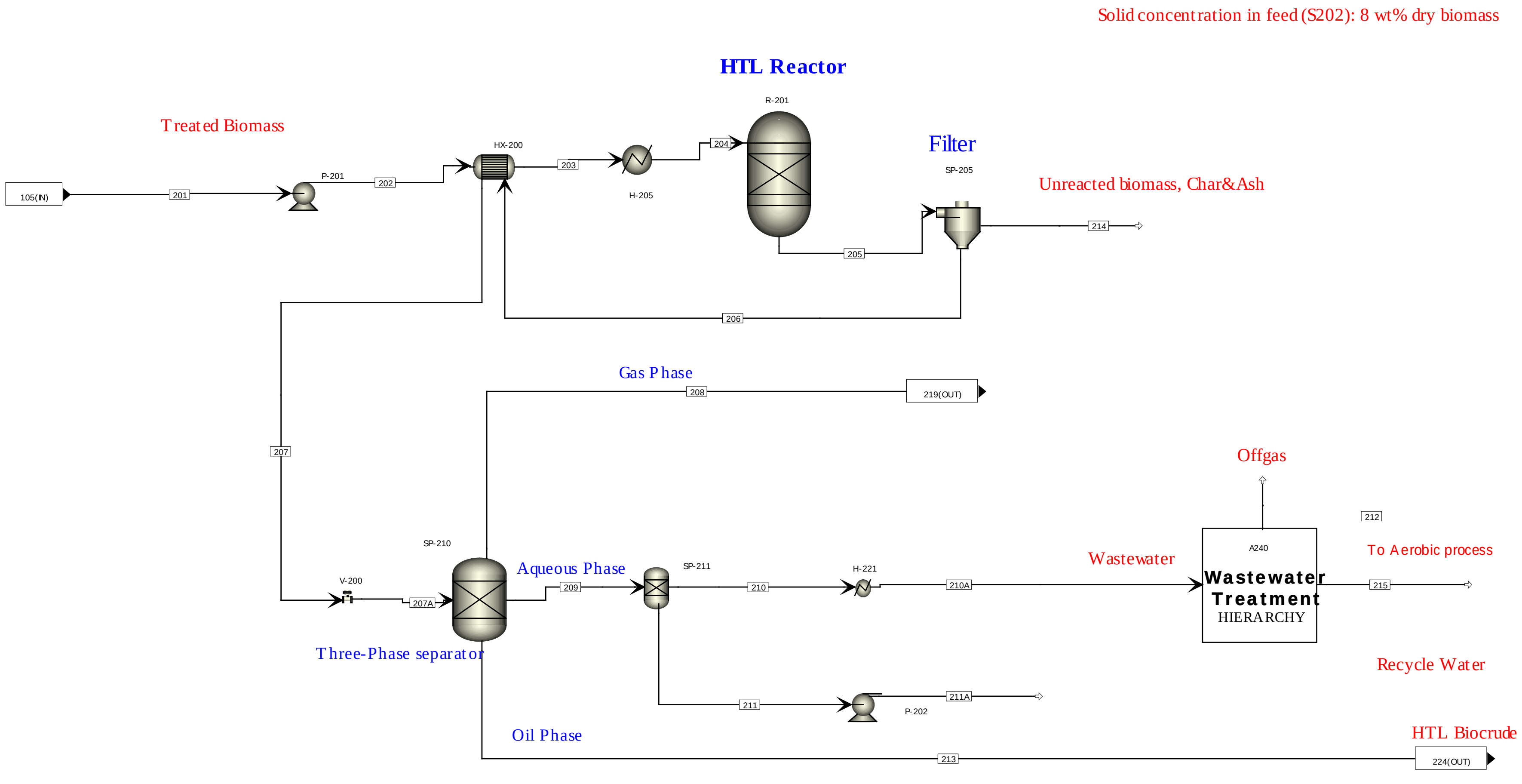

Figure 9. Hydrothermal Liquefaction and Subsequent Product Separation Process

The recovered biocrude phase consists mainly of oxygenated hydrocarbons and a certain percentage of moisture, as is represented in **Table 9**. The model assumes that all the ash is separated with the solids, which is an over-simplification of the process, as some ash components will be soluble in the aqueous. The biocrude stream is processed further through hydrodeoxygenation for the production of the finished liquid hydrocarbon product.

Table 9. Liquid Product Composition

Biocrude Components	wt%
Organics	95.5
Water	5.5
Ash	0
Aqueous Phase Components	wt%
Process water + reaction water	96.9
Dissolved organics	3.1
Ash	0

The recovered aqueous phase consists mostly of the water used to form the feed slurry, but also contains dissolved aqueous phase organics -- alcohols, acids, and other oxygenates. The majority of this stream is recycled for slurry formation in the feed pretreatment section. The balance (about 5%) is sent to wastewater treatment, which includes anaerobic digestion (AD). In the AD reactor the organics found in the aqueous stream are converted to CH_4 and CO_2 which is sent to the hydrogen plant where it is used as reformer feedstock as well as fuel gas for fired heaters. The surplus is sent to the boiler to generate process steam.

The gas product (shown in **Table 10**) includes carbon dioxide (CO_2), methane (CH_4), and a little hydrogen (H_2) and other light hydrocarbon gases (ethane, propane, butane). These products are assumed to be sent to the hydrogen plant for hydrogen production.

Table 10. Gas Phase Composition

Gas Component	volume %
CO_2	90.2
CO	0
CH_4	3.0
H_2	0.9
Ethane	2.5
Propane	1.9
Butane	1.5

In the biocrude hydrotreating section, the biocrude is reacted with hydrogen gas over a catalyst until oxygen content below 1% is achieved. The resulting hydrocarbon oil has a wide boiling range from lighter than gasoline to heavier than diesel. Similar to the fast pyrolysis case, the hydrocarbon products boil in the gasoline, diesel, and heavy hydrocarbon ranges.

3.3 Liquid Product Upgrading by Hydroprocessing

The upgrading process models for the fast pyrolysis process and the hydrothermal liquefaction process are similar. Also the hydrogen plant is designed on the same basis in both models.

Liquids produced from biomass by direct liquefaction (e.g. fast pyrolysis or hydrothermal liquefaction) can be upgraded through a catalyzed reaction process where the oxygenated product is exposed to hydrogen under elevated pressure and high temperature[22]. This process reduces the oxygen content via hydrodeoxygenation and decarboxylation reactions such that the resulting concentration is below 1% while also bringing much of the product into the appropriate molecular weight range for useful liquid fuels. The end result improves the overall value and usability of the finished product. Hydroprocessing is conducted in a continuous-flow, fixed-bed reactor packed with catalyst. The reactor effluent is then distilled into to gasoline, diesels and heavy fuel fractions as depicted in **Figure 10.** Distillations represented in this model are hypothetical and based on previous work and literature findings[9].

In this part of the process, the bio-oil is pumped to 13.6 MPa and combined with compressed hydrogen from the hydrogen plant. The mixture is preheated by heat exchange with the hydrotreating reactor effluent and sent to the hydrotreating system. The experimental liquid hourly space velocity used in the HTL case is 0.15 volume of oil per volume of catalyst bed per hour. The bio-oil is almost completely converted at 400 °C to light hydrocarbons, some C_1-C_3, mainly C_4 to C_{17}, and a small fraction of heavier components. Although many similarities exist in the upgrading of fast pyrolysis bio-oil and hydrotreating of HTL biocrude, there are some key differences as well. The nature of the bio-oil feed to the HDO reactor and the number of stages needed for each process to achieve similar products differ in the FP and HTL cases. HTL biocrude contains a significantly lower concentration of oxygen before upgrading and is more thermally stable therefore it can be adequately processed in one stage of HDO utilizing a conventional sulfided NiMo catalyst. However, FP bio-oil is more oxygenated and thermally reactive, therefore several stages have to be employed for stabilization and upgrading to achieve a finished product[9]. These were specified as Ru/C in the stabilization, sulfided Ru/C in the first stage hydrotreater, and sulfided NiMo in the second hydrotreater. Space velocities for the three steps are 0.5, 0.22 and 0.22, respectively. The operating conditions and production yields for the hydrotreating reaction simulation were based on the experimental tests for both the FP[23] and HTL models.[24] Costs and energy demands are therefore different for the two cases and the differences lead to different outcomes in the techno-economic assessment.

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[22] Elliott, D.C. Historical Developments in Hydroprocessing Bio-oil. *Energy Fuels* **2007** 21:1792-1815.

[23] Jones, S.B.; Snowden-Swan, L.L. *Production of Gasoline and Diesel from Biomass via Fast Pyrolysis, Hydrotreating and Hydrocracking: 2012 State of Technology and Projections to 2017*. PNNL-22684, Pacific Northwest National Laboratory, Richland, Washington, February **2013**.

[24] Zhu, Y. et al. Techno-economic analysis of liquid fuel production from woody biomass via hydrothermal liquefaction (HTL) and upgrading. *Applied Energy,* accepted for publication **2014.**

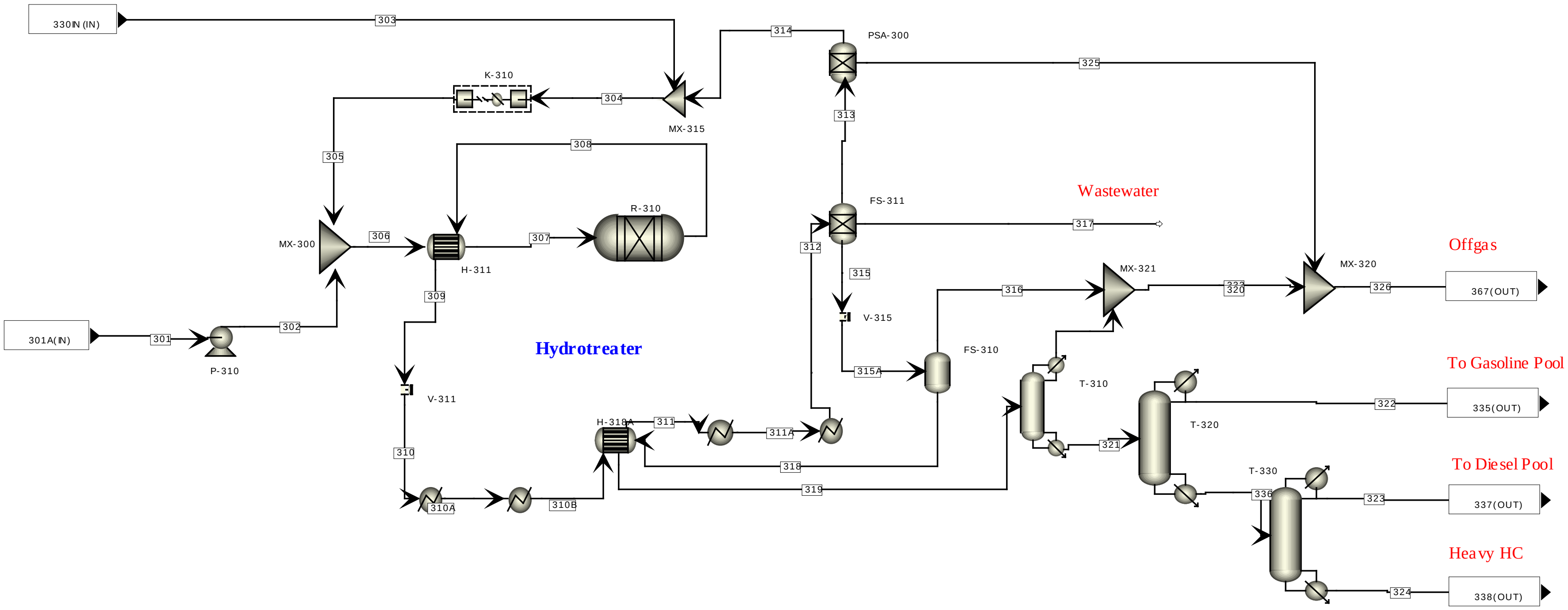

Figure 10. Hydrodeoxygenation and Distillation to Fuels Process

The effluent from the hydrotreating reactors is cooled by pre-heating the reactor inlet stream. The effluent is further cooled by other process streams, then air, and finally trim cooled with cooling water. The cooled effluent is separated into product oil, wastewater, and off-gas streams. The off-gas from the hydrotreaters is sent to a Pressure Swing Adsorption (PSA) system and 80% of hydrogen in the feed is assumed be recovered. This assumption is based on current cost information for a PSA unit which can operate at this recovery efficiency. The recovered hydrogen is mixed with makeup hydrogen and compressed to feed back to the reactors. The low pressure PSA tail gas stream, which is not rich in hydrogen and but contains reformable light hydrocarbons, is sent to the hydrogen plant for hydrogen production.

The hydrotreated oil is then further processed by removing butane and lighter components in a lights removal column. This column also serves to adjust the initial boiling point of the gasoline fraction. The overhead gas containing light organics is used as hydrogen plant feedstock. The hydrotreated oil is further separated into gasoline and diesel range fuels, and a heavy fraction which boils above 400°C. In this case, the gasoline, diesel, and heavy boiling range fraction are assumed to be the final fuel blend-stock product.

3.4 Hydrogen plant

Hydrogen for the bio-oil upgrading process is produced by steam reforming in an onsite hydrogen plant. The hydrogen plant mainly relies on off-gas from the biomass conversion processes and upgrading processes, or from the anaerobic digestion wastewater treatment for the hydrothermal liquefaction case.

The gas mixture is pre-heated with heat from the reformer furnace while wastewater from the biomass conversion processes and the upgrading processes is heated with the reformer furnace flue gases to saturated steam. Steam is mixed into the pre-heated gas mixture and sent to the reformer which operates at 3.1 MPa and 850 °C. The reformed gas is cooled down and then undergoes a water-gas shift reaction in a separate shift reactor in order to further increase hydrogen production. The reformed gas goes through a knock-out for water removal and hydrogen is separated in a PSA unit before it is sent to the bio-oil upgrading reactor. The condensed water from the knock-out is mixed with hydrotreater wastewater and used for steam production in a recycle loop. Such reuse of the hydrotreater water as reformer feed needs to be validated. The remaining gas after hydrogen is separated in a pressure-swing adsorption (PSA) process is sent to the reformer furnace for combustion.

4.0 Process Mass and Energy Balances

Using Aspen Plus® models, overall mass and energy balances could be generated for the processes of interest based on versions developed by the participants in earlier research efforts. For each process option a new model was developed for use in the analysis. Each model was based on relevant information including technical information from literature as well as experimental values. In order to develop comparable models for fast pyrolysis with upgrading and hydrothermal liquefaction with hydrotreating, several key challenges were addressed. The initial models had different sets of compounds chosen to represent primary and upgraded products. Furthermore, the ultimate analysis of the forest residue biomass feedstock was not the same in each model. Fast pyrolysis bio-oil, when compared to HTL biocrude, is markedly different in oxygen content as well as water content. Therefore, it was necessary that the model compound sets used to represent the two primary products were somewhat different. In order to facilitate some comparison between the two primary liquid products several key compounds were chosen to appear in the composition of both. Due to these changes new mass balances surrounding the FP and HTL reactors were developed as appropriate inputs based on the mole flow of C, H, O, N and S, specified by the new model compounds in the products.

Similarly in the upgrading section of each model, mass balances were developed to calculate mole flow of C, H, O, N and S coming in as primary liquid and leaving as upgraded oil, gas, and solids. Detailed mass balances were calculated in an Excel-based calculator defining the RYield reactor block output. Molecular flow rates for C, H, O, N and S were calculated based on laboratory data and balanced against chosen model compounds, which would represent the finished fuel products. Composition of the final product was nearly the same for both models. Excel Solver (Linear Program Function) was used to determine possible answers for 16 equations with 16 unknowns.[25] Solver is an Excel based analysis tool used for optimization of data. Solver helps to find an optimal value in one cell (referred to as the target cell) based on restrictions and the desired outcome such as an overall mass balance of reactants and products. The function works by changing a group of cells related to the target cell to find the desired optimal value. In this particular case Solver is used to determine the best mass rate of 10+ products such that all atoms (C, H, O, N and S) are balanced with respect to the reactants. Specifically in this model this technique was used in developing a balance around the Hydrotreating reactor in the upgrading area of both processes. Because the makeup of both the unprocessed bio-oil or biocrude and the finished product includes many constituents this was an optimal way to develop a mass balance around the reactor which is a necessary output for Aspen Plus.

However before a realistic composition of finished fuel was produced, a first “best-guess” estimate of the flow rates for each constituent had to be made. If the Solver function is used without the initial guess it can come up with unrealistic solutions which can satisfy the constraints of a complete material balance but are not useful for implementation in the model (i.e. negative flow rate). That is why when a plausible solution was found the final fuel product values produced by the Solver method was correlated with known finished fuel simulated distillation (Simdist) information. The constricting data to solve these equations included the elemental mass balance (mass of elements coming in had to equal the mass of elements exiting the reactor), the production of water, which is measured experimentally, as well as

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[25] The implementation of the Solver analytical method used was developed by Aye Meyer at PNNL

setting the oxygen content of the final product oil to below 1%. Furthermore, a starting point for the plausible distillation curve of the finished products was developed and compared to Gas Chromatography Simulated Distillation data developed on upgraded products at PNNL. The method used, ASTM D2887, was developed for diesel fuel testing, and, therefore, is still being refined for other products, but was used here as a starting point for addressing the validity of the model product composition. Solver function solutions were achieved and the resulting compound yields were used in the process models.

4.1 Mass Balance for Fast Pyrolysis and Upgrading

The mass balance for fast pyrolysis and bio-oil upgrading is depicted in **Figure 11**.

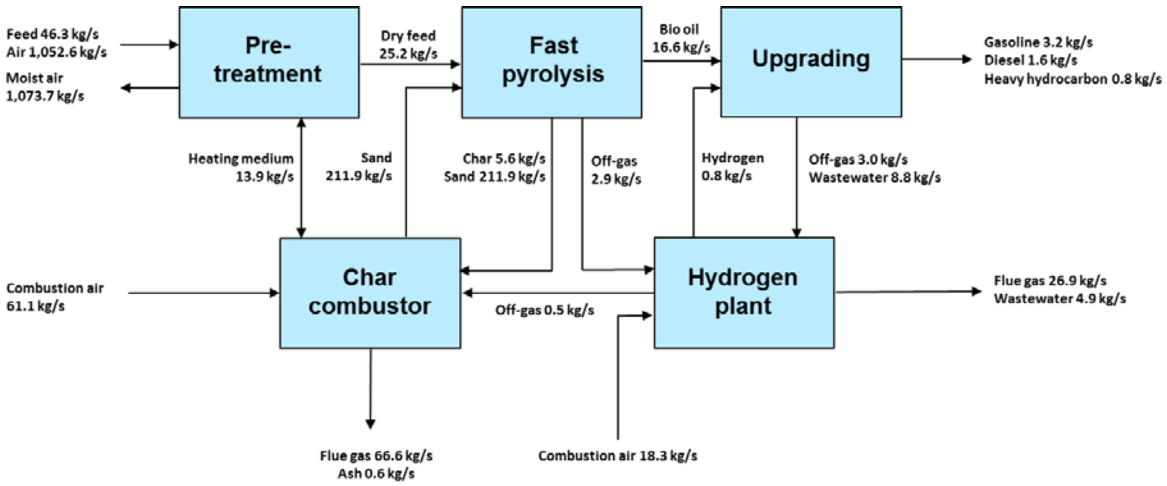

Figure 11. Mass Balance for the Fast Pyrolysis

The tabular form of the mass balance data for fast pyrolysis and bio-oil upgrading is given in **Table 11.** The overall mass balance for fast pyrolysis and upgrading shows a 24% yield (5.6/23.15 kg/s) of hydrocarbon liquids on a dry biomass basis.

Table 11. Mass Balance for the Fast Pyrolysis Pathway

Mass balance fast pyrolysis, kg/s	IN	OUT
Wet forest residue	46.3	
Combustion air	79.4	
Flue gas		93.5
Moisture		21.1
Gasoline		3.2
Diesel		1.6
Heavy hydrocarbon		0.8
Wastewater		4.9
Ash		0.6
TOTAL	125.7	125.7

4.2 Energy Balance for Fast Pyrolysis and Upgrading

The energy balance for fast pyrolysis and bio-oil upgrading is depicted in **Figure 12**.

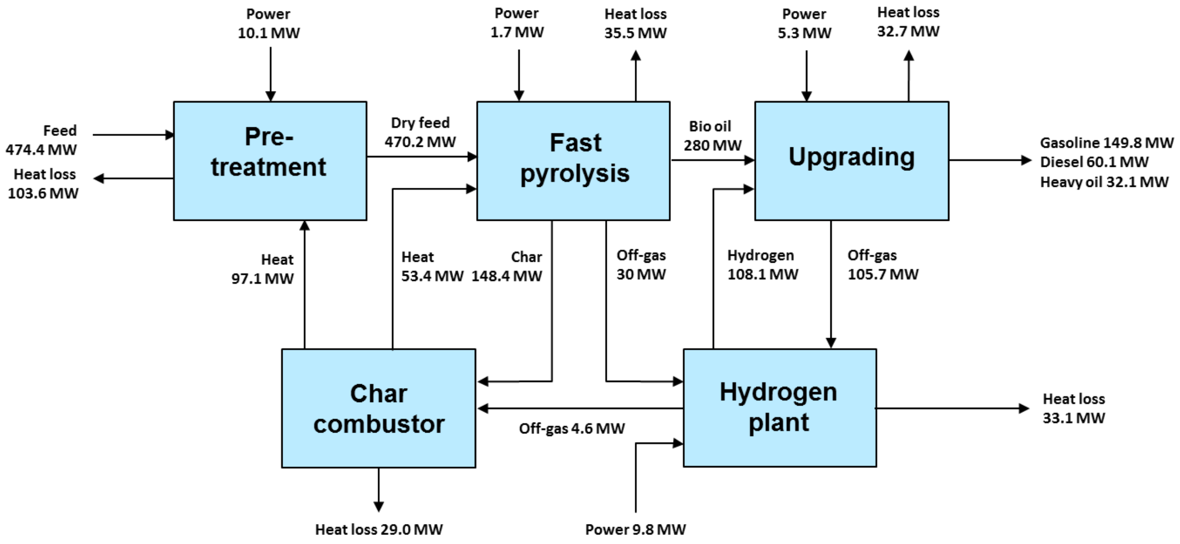

Figure 12. Energy balance (HHV basis) for Fast Pyrolysis

The overall energy balance for the fast pyrolysis process is off by 3.9%. This is largely related to the hydroprocessing product specification and the choice of model components for this part of the model. The energy balance for other individual blocks range within a window of 0.04 – 0.5%.

The lower heating values for calculating the overall process efficiency for fast pyrolysis and upgrading are given in **Table 12.** The overall energy efficiency of fast pyrolysis and upgrading shows a 54.4% yield of hydrocarbon liquids based on feed and power inputs. The Power inputs are calculated by Aspen-Plus and are reported here without adjustment between electrical and thermal energy.

Table 12. Input and output for Fast Pyrolysis based on LHV

Energy balance fast pyrolysis, LHV, MW	IN	OUT
Feedstock	387.5	
Power	27.0	
Gasoline		139.4
Diesel		55.5
Heavy hydrocarbon		30.5
Heat loss		189.1
TOTAL	414.5	414.5

4.3 Mass Balance for Hydrothermal Liquefaction and Hydrotreating

The mass balance for hydrothermal liquefaction and biocrude hydrotreating is depicted in **Figure 13**.

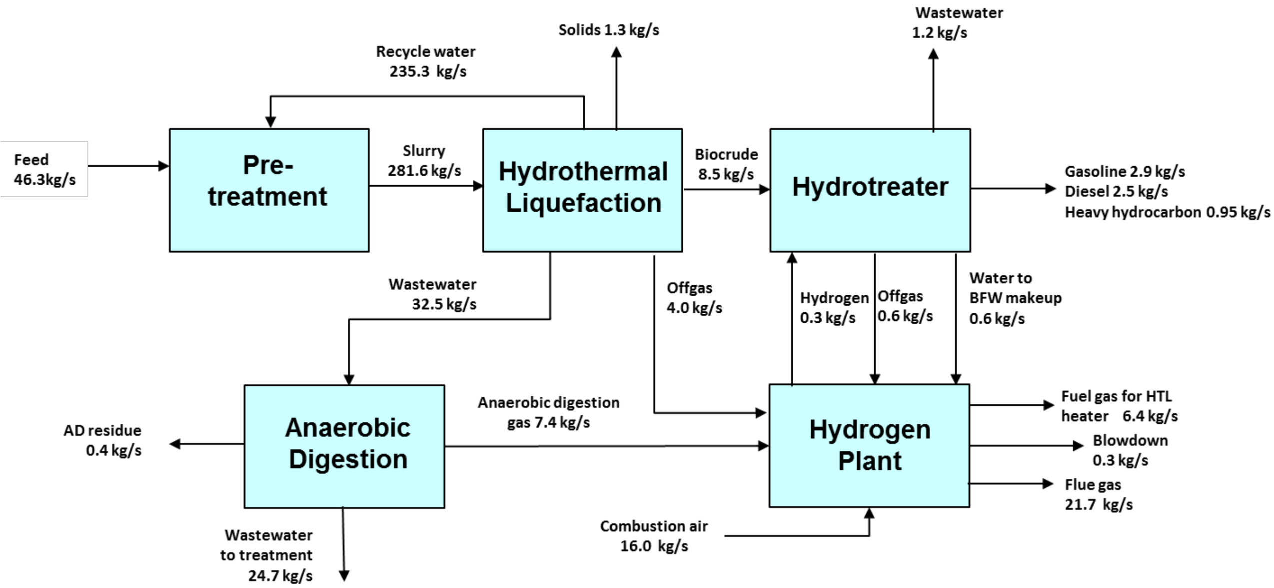

Figure 13. Mass Balance for HTL and Upgrading Process

The tabular form of the mass balance data for hydrothermal liquefaction and hydrotreating is given in **Table 13.** The overall mass balance of hydrothermal liquefaction and hydrotreating shows a 27% yield (6.35/23.15 kg/s) of hydrocarbon liquids on a dry biomass basis.

Table 13. Mass Balance for the Hydrothermal Liquefaction Pathway

Mass balance hydrothermal liquefaction, kg/s	IN	OUT
Wet Forest residue	46.3	
Combustion air	16.0	
Flue gas		21.7
Fuel gas		6.4
Gasoline		2.9
Diesel		2.5
Heavy oil		0.95
Wastewater		25.9
Solids		1.3
AD Residue		0.4
Blowdown		0.3
TOTAL	62.3	62.3

4.4 Energy Balance for Hydrothermal Liquefaction and Hydrotreating

The energy balance for hydrothermal liquefaction and biocrude hydrotreating is depicted in **Figure 14.**

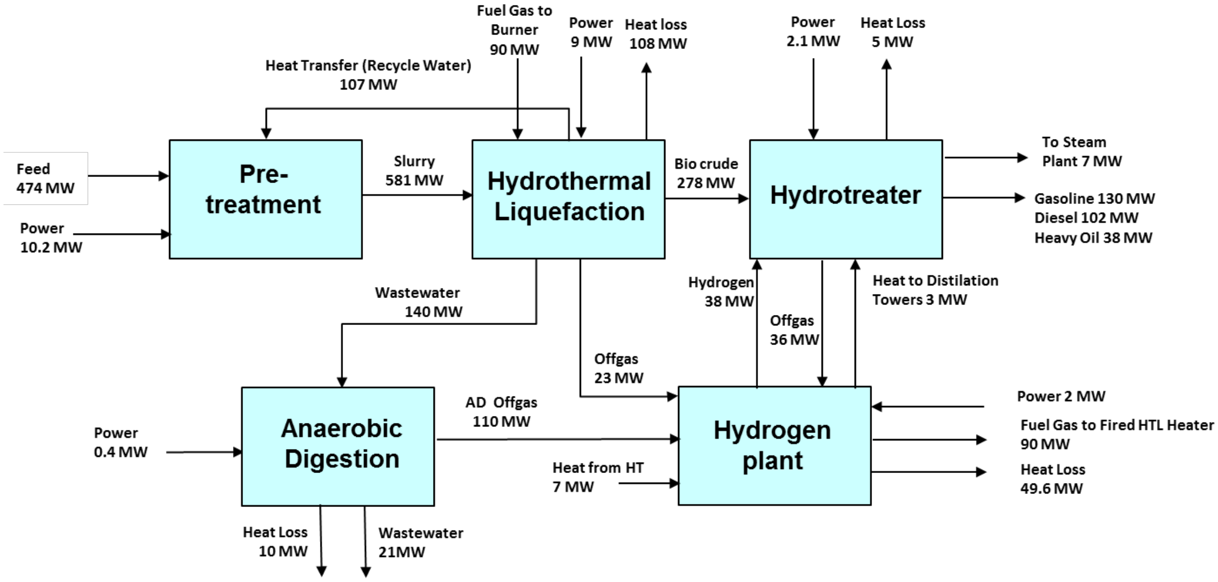

Figure 14. Energy balance (HHV basis) for HTL

The overall energy balance for the HTL process is off by 4.2%. This is largely related to the hydrothermal liquefaction product specification and the choice of model components for this part of the model. The energy balance for other individual blocks range within a window of 0.2 – 3.5%.

The tabular form of the energy flow data for hydrothermal liquefaction and hydrotreating is given in **Table 14**. The overall energy efficiency of hydrothermal liquefaction and hydrotreating shows a 62.3% yield of hydrocarbon liquids based on feed and power inputs. The Power inputs are calculated by Aspen-Plus and are reported here without adjustment between electrical and thermal energy. There is an excess steam product, which is unlikely to be useful for byproduct power production, and so is relegated to heat loss.

Table 14. Energy balance for Hydrothermal Liquefaction based on LHV

HTL Energy Flows, LHV, MW	IN	OUT
Feedstock	387.5	
Power	23.7	
Gasoline		121.7
Diesel		97.6
Heavy Oil		36.8
Heat Loss		155.1
Total	411.2	411.2

5.0 Comparative Analysis of Life Cycle GHGs

Life cycle greenhouse gas emissions (GHGs) are estimated for fuels from the fast pyrolysis and upgrading pathway and the HTL and hydrotreating pathway. Shown in **Figure 15**, the scope of the fuel cycle includes feedstock production through final fuel consumption in an automobile. The functional unit for the analysis is grams of CO_2-equivalent per MJ fuel consumed (g CO_2-e/MJ).

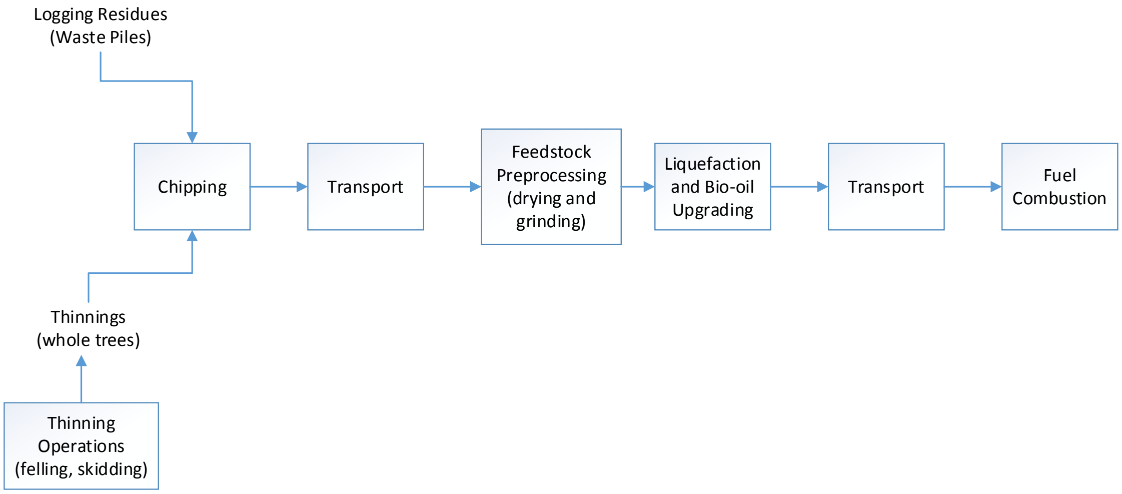

Figure 15. Life cycle of fuels produced from liquefaction of woody feedstocks and bio-oil upgrading.

5.1 Methods

The SimaPro software[26] is used to model and estimate cumulative GHGs and energy use for the fuel cycle. A 50/50 mixture of two woody feedstocks, logging residues and forest thinnings, is analyzed. The nature of these feedstocks and differences between the two are discussed more in the feedstock production section. It is assumed that the carbon released to the atmosphere during the conversion and fuel combustion stages is equal to that taken up from the atmosphere during growth of the trees, and therefore biogenic carbon is not tracked in the analysis (with the exception of any biogenic methane emitted during these stages, which is accounted for in the analysis). This is in agreement with the most recent version of the IPCC GWP 100 impact assessment method included in SimaPro 8. Temporal changes in forest carbon stocks associated with forest residue removal are assumed to be negligible, as discussed in more detail in the feedstock production section.

5.1.1 Feedstock Production

As shown in **Figure 15**, a mixture of logging residues and forest thinnings (50/50) is considered as feedstock for the liquefaction technologies. A variety of approaches have been taken with regard to allocation of burdens and consideration of potential changes in forest carbon stocks associated with removing residues for bioenergy production. Woody residues resulting from forest treatments in the U.S.

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[26] SimaPro Life Cycle Assessment Software, v. 8.0. Amersfoort, the Netherlands: Product Ecology Consultants, 2013.

have historically been burned onsite.[27] As such, this material is most often treated as a waste product, receiving only the burdens of collection and necessary preprocessing (e.g., chipping) to prepare the feedstock for transport from the landing to the refinery.[28] Others consider the residue to be a co-product of the forest stand that is purposely grown for both timber and bioenergy, and as such allocate a portion of the burdens of growing and harvesting timber to the residues.[29] Recent studies on the potential GHG implications of increased residue removal argue that in the short term, GHG emissions are higher with immediate conversion/combustion of forest residues as compared to if the residues were left to decay more slowly over time.[30] However, others argue there is no significant change in forest carbon stock over the long term with a sustainable level of residue removal. For this analysis, the following assumptions are made for the forest feedstocks:

- Forest residue is a waste product of logging operations and consists of the unmerchantable parts of harvested trees, e.g., tops, small branches, and leaves, that are piled up and either left to decompose or burned on the forest floor as part of forest management. As such, this feedstock does not carry any environmental burdens associated with the harvested timber.

- Forest thinnings consist of whole trees that are removed as part of forest management operations to enhance growth and manage fire risk. As such, this feedstock carries the full burdens of thinning operations.

- Extra fertilizer is not required as a result of residue removal.

- Soil carbon losses due to removal of residue and thinnings are not considered in the analyses.

Both residues and thinnings are assigned the burdens of chipping at the landing prior to transportation. The diesel usage for each stage of feedstock collection comes from Johnson et al.[27] and is shown in **Table 15**. The chipper used for logging residues is a horizontal grinder, which requires a hydraulic loader. Forest thinnings are processed with a whole tree chipper, which skids whole trees directly onto the chipper bed and therefore does not require a separate loader. Note that more fuel is consumed for chipping residues with a horizontal grinder than for chipping thinnings with a whole tree

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[27] Johnson, L, B Lipke, and E Oneil. 2012. “Modeling Biomass Collection and Woods Processing Life-Cycle Analysis,” Forest Prod. J. 62(4): 258-272.
Jones, G., D. Loeffler, D. Calkin, and W. Chung. 2010. “Forest treatment residues for thermal energy compared with disposal by onsite burning: Emissions and energy return,” Biomass and Bioenergy 34: 737-746.

[28] Daystar, J, C Reeb, R Venditti, R Gonzalez, and ME Puettman. 2012. “Life-Cycle Assessment of Bioethanol from Pine Residues via Indirect Biomass Gasification to Mixed Alcohols,” Forest Prod. J. 62(4):314-325. Forest Products Society. Lipke, B, ME Puettman. 2013. “Life-Cycle Carbon from Waste Wood Used in District Heating and Other Alternatives,” Forest Prod. J. 63(1/2): 12-23. Forest Products Society. Hsu, D.D. 2012. “Life cycle assessment of gasoline and diesel produced via fast pyrolysis and hydroprocessing,” Biomass and Bioenergy 45:41-47.

[29] Dias, A.C. 2014. “Life cycle assessment of fuel chip production from eucalypt forest residues,” Int J Life Cycle Assess, 19:705-717. Sorsa, R. and S. Soimakallio. 2012. “Does bio-oil derived from logging residues in Finland meet the European Union greenhouse gas performance criteria?” Energy Policy, http://dx.doi.org/10.1016/j.enpol.2012.10.056.

[30] Repo, A, H Böttcher, G Kindermann, and J Liski. 2014. “Sustainability of forest bioenergy in Europe: land-use-related carbon dioxide emissions of forest harvest residues,” GCB Bioenergy, doi: 10.1111/gcbb.12179. John Wiley & Sons Ltd. Domke, G.M., D.R. Becker, A.W. D’Amato, A.R. Ek, and C.W. Woodall. 2012. “Carbon emissions associated with the procurement and utilization of forest harvest residues for energy, northern Minnesota, USA,” Biomass and Bioenergy 36: 141-150.

chipper. Emissions associated with equipment production and maintenance aren't included in the analysis.

Table 15. Feedstock harvesting and collection assumptions.

Feedstock Collection Process	Diesel Consumption, L/dry tonne	
	Logging Residue[1]	Forest Thinnings[1]
Feller	0	0.81
Skidder	0	2.64
Loader	0.82	N/A
Chipper	3.01	1.3
Total	3.83	4.75

[1]Johnson et al. 2012. (ref #27)

5.1.2 Feedstock Transportation

After chipping, wood chips are transported from the forest landing 75 miles to the biorefinery.[27] A transport process from the EcoInvent database,[31] "operation, lorry 16-32t, EURO5", is used to model the emissions of feedstock transport. The process assumes 0.21 kg fuel/km for the lorry operation. Fuel consumption associated with the return trip back to the forest is not included in the analysis.

5.1.3 Feedstock Handling and Preprocessing at the Refinery

At the biorefinery, wood chips are unloaded and then cleaned with an electromagnet.[32] Equipment is also necessary for control and collection of dust produced during handling and processing. For the pyrolysis pathway, the chips are dried using waste heat from the char combustor and then ground to a powder of 2 mm or less to meet the reactor feed specification. For the HTL pathway, the chips are not dried, but are instead ground at 50% moisture content. Grinding energy is taken from Rensfelt et al[33] for 8% moisture content wood flour production. As data on grinding of green wood could not be obtained from the literature, it is assumed that the grinding energy needed for both pathways is equal. HTL does not require as small of particle size as fast pyrolysis, and thus, the increased energy required for moist wood may be somewhat offset by lower energy required for larger particle size. Energy consumption values and associated references for the feedstock grinding and handling steps are given in **Table 16**.

5.1.4 Conversion

Mass and energy balance information from the process models, along with life cycle inventory data from the EcoInvent[31] and U.S. Life Cycle Inventory[34] databases is used to populate the model. Key

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[31] EcoInvent 2011. EcoInvent Database Version 2.2, Hamburg, Germany: Swiss Center for Life Cycle Inventories.

[32] Searcy and Hess. 2010. "Uniform-Format Feedstock Supply System: A Commodity-Scale Design to Produce an Infrastructure-Compatible Biocrude from Lignocellulosic Biomass," INL/EXT-10-2037 Revision 0.

[33] Rensfelt, Lindman, Bjerle, Kelen: Raport inom NE-området Syntetiska drivmedel, Project PDU. Slutrapport. 80-04-15 KTH.

[34] U.S. Life Cycle Inventory Database. 2012. National Renewable Energy Technology Laboratory. https://www.lcacommons.gov/nrel/search.

assumptions are given in **Table 17**. Catalyst consumption is scaled based on flows from Jones et al.[35] In the absence of life cycle inventory data for actual hydroprocessing catalysts (for example, specific CoMo

Table 16. Feedstock handling and preprocessing assumptions.

Processing Step	Energy Consumption	Reference
Grinding energy	71.2 kwh/dm tonne	#33
Handling, dust collection, chip cleaning	5 kwh/dm tonne	#32
Front-end loader	0.42 L diesel/dm tonne	#32
Electricity Grid Mix		#31
Coal	50%	
Nuclear	20%	
NG	17%	
Renewable	10%	
Oil/Industrial gas	3%	

Table 17. Conversion stage assumptions for 2000 dry tonne/day biorefinery.

	Fast Pyrolysis and Upgrading	HTL and Hydrotreating
Fuel Products LHV, MJ/kg		
Gasoline	43.6	42.1
Diesel	35.1	39.2
Heavy oil	39.7	38.8
Fuel Products Flow, kg/hr		
Gasoline	11498	10408
Diesel	5697	8957
Heavy oil	2767	3414
Allocation to Fuels (by energy content), %		
Gasoline	62	48
Diesel	25	38
Heavy oil	14	14
Net electricity for plant, MW (excluding grinding energy, see Table 16)	21.07	17.76
Electricity grid mix, %[31]	(see Table 2)	
Catalyst Type	Zeolite (proxy in absence of data for actual catalysts)	
Catalyst Lifetime, years[35]		
Hydrotreating	1	
Hydrocracking	1	
Steam Reforming	3.5	
Catalyst sulfiding agent	Dimethyl sulfoxide (proxy for dimethyl sulfide)	
Dimethyl sulfide use, kg/hr[35]	23	
Wastewater, kg/hr	17640	94320

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[35] Jones, S., P. Meyer, L. Snowden-Swan, A. Padmaperuma, E. Tan, A. Dutta, J. Jacobson, and K. Cafferty. 2013. “Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels: Fast Pyrolysis and Hydrotreating Bio-oil Pathway,” PNNL-23053NREL/TP-5100-61178.

and Ru based formulations), a zeolite product from the EcoInvent database ("zeolite, powder, at plant/RER with US electricity U") is used as a proxy. The actual hydrotreating catalysts may have a very different GHG impact than that approximated with zeolite, depending on the specific metals used (e.g., precious metals) and their loadings, as well as the level of regeneration and/or reclamation that occurs as part of spent material management. Sulfiding agent consumption is scaled based on flows from Jones et al.[35] It is assumed that the sulfiding agent is dimethyl sulfide and in the absence of life cycle inventory for this compound, dimethyl sulfoxide from the EcoInvent database ("dimethyl sulfoxide, at plant/RER with US electricity U") is used as a proxy. As dimethyl sulfoxide is produced commercially via oxidation of dimethyl sulfide, this is a conservative estimate of life cycle inventory for dimethyl sulfide.

5.1.5 Fuel Distribution and Consumption

Emissions associated with fuel distribution to the end user (fuel transportation and operation of storage tanks and fueling stations) are modeled using an EcoInvent database process ("petrol, unleaded, at refinery/kg/RER/U"). Emissions of biogenic methane and N_2O from combustion of gasoline and diesel fuel in a vehicle are adapted from GREET.[36]

5.2 Results

Shown in **Figure 16** are the estimated life cycle GHGs for fuels from the fast pyrolysis and HTL conversion pathways. Emissions for HTL are lower than for pyrolysis due to lower electricity consumption, as shown in **Figure 17**. The difference in plant electricity consumption stems primarily from the fact that HTL oil is less oxygenated than pyrolysis oil, and therefore requires less hydrogen (and power to compress the hydrogen) for upgrading per unit of fuel energy produced. In addition, fuel yield is about 14% higher for HTL than for pyrolysis, resulting in lower energy consumption per unit fuel for conversion as well as for feedstock production, transport and preprocessing stages. Emissions reductions for both technology routes are over 60% relative to the 2005 baseline for petroleum based gasoline and diesel.[37] The results suggest these fuels meet the Energy Independence and Security Act of 2007 Renewable Fuel Standard (RFS2)[38] cellulosic biofuel definition, however, final qualification is made by the EPA based on their independent analysis and determination.

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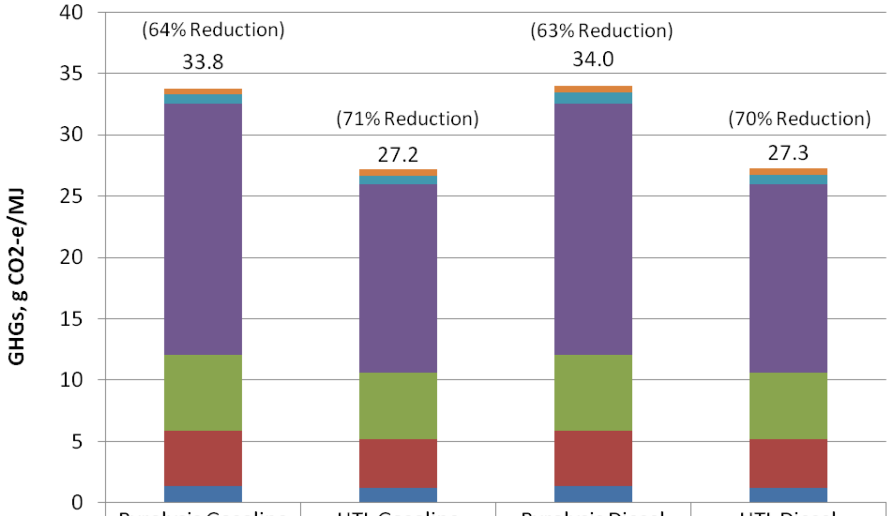
[36] GREET Model, The Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation Model, 2013. Argonne National Laboratory, Chicago, IL.

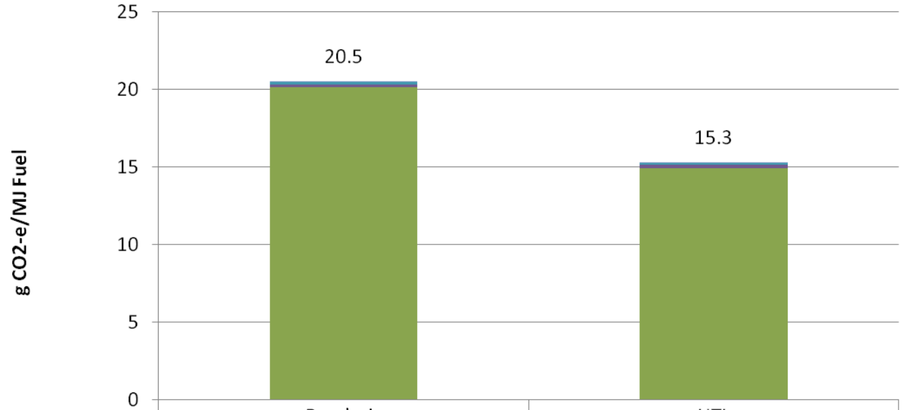
[37] U.S. EPA, Docket # EPA-HQ-OAR-2005-0161-3173. 2010. "Fuel-Specific Lifecycle Greenhouse Gas Emissions Results," Accessed at http://www.regulations.gov/#!documentDetail;D=EPA-HQ-OAR-2005-0161-3173.

[38] Code of Federal Regulations, 42 USC 7545. 2007. Energy Independence and Security Act. Public Law 100-140.



	Pyrolysis Gasoline	HTL Gasoline	Pyrolysis Diesel	HTL Diesel
🟧 Fuel Use in Vehicle	0.49	0.49	0.52	0.52
🟦 Fuel Distribution	0.73	0.75	0.90	0.80
🟪 Conversion	20.50	15.32	20.50	15.32
🟩 Feedstock Preprocessing at Biorefinery	6.21	5.46	6.21	5.46
🟥 Feedstock Transport	4.46	3.93	4.46	3.93
🟦 Feedstock Production	1.38	1.21	1.38	1.21
Total	33.8	27.2	34.0	27.3

Figure 16. Life cycle GHG emissions for fuels from liquefaction and upgrading for forest residue/forest thinnings mixture (50/50). Percent reduction is relative to the 2005 petroleum baseline GHGs calculated for the RFS2, 93.08 g CO_2-e/MJ and 91.94 g CO_2-e/MJ for gasoline and diesel, respectively[37]



	Pyrolysis	HTL
🟦 Waste Treatment	0.02	0.05
🟧 Boiler/Cooling Chem	0.001	0.001
🟦 Infrastructure	0.18	0.16
🟪 Catalyst + Sulfide Agent	0.16	0.17
🟩 Electricity	20.14	14.94
Total	20.5	15.3

Figure 17. Conversion stage partial life cycle GHG emissions for fuels produced from liquefaction and bio-oil upgrading.

6.0 Cost Estimation

6.1 Capital Equipment Costs

The capital cost estimate is determined by aggregating individual equipment costs and applying factors. The equipment costs used in the economic analysis were developed from existing sources by extrapolation to appropriate scale of stream flow. Individual equipment costs were not developed within this study. The equipment cost estimates for fast pyrolysis were derived from Jones et al.[23], which used a 400 t/d reactor size, by adjusting the equipment based on the feed rate in this study (4 X 500 t/d) using a 0.7 power factor. The uninstalled costs are the summation of equipment estimates. The installed costs (Fixed Capital Investment, FCI) are calculated from the equipment costs with a range of relevant factors applied for the different types of equipment by Jones et al.[23] Installation factors used in the cost analysis of the equipment were obtained by several methods. Primary sources include Harris Group[39], SRI PEP 2007 Yearbook[40] as well as Aspen Capital Cost Estimator.[41] Values were either obtained directly or calculated based on equipment costs provided by the source.

6.2 Production Costs

Annual production cost is evaluated by adding operation and capital costs. Operation cost includes fixed and variable terms. Capital costs are estimated based on annuity.

Capital to be depreciated and used as part of production cost estimate is derived from the above fixed installed capital investment (FCI) costs by adding estimates for start-up costs (10 % of FCI), and interest during construction. A two year construction time is assumed.

Fixed operating costs include:

- operating labor (which is a function of plant size, 5 shifts assumed, 6 persons per shift)
- maintenance labor (1 % of FCI assumed)
- overheads (2 % of FCI assumed)
- maintenance materials (3 % of FCI assumed)
- taxes, insurance (2 % of FCI assumed)
- other fixed costs (1 % of FCI assumed)

Variable operating costs include:

- feedstock cost
- natural gas
- electricity consumption
- catalyst costs
- waste handling

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[39] Dutta, A., Talmadge, M., Hensley, J., Worley, M., Dudgeon, D., Barton, D., Groenendijk, P., Ferrari, D., Stears, B., Searcy, E., Wright, C., Hess, J.R. **2011**. *Process design and economics for conversion of lignocellulosic biomass to ethanol: thermochemical pathway by indirect gasification and mixed alcohol synthesis.* Golden, CO: National Renewable Energy Laboratory. http://www.nrel.gov/docs/fy11osti/51400.pdf

[40] SRI 2007. “Hydrogen production from natural gas ” PEP Yearbook, Vol 1E, SRI International, Menlo Park, California.

[41] http://www.aspentech.com/products/aspen-icarus-process-evaluator.aspx

Parameters used in the assessment are summarized in **Table 18** below.

Table 18. Parameters used in economic assessment

Feedstock forest residue cost	30	$/t (50% moisture)
	12.9	$/MWh
Electricity	6.9	¢/kWh
Wastewater	0.73	$/t
Labor rate	0.05	M$/a
Interest rate	10	%
Service life	20	a
Annuity	0.1175	
Interest during construction	11	%
Annual operating time	7000	h/a
Ru/C catalyst	132	$/kg
NiMo catalyst	75	$/kg

6.3 Fast Pyrolysis and Bio-oil Upgrading Process Costs

The capital costs are grouped into the subsections of the process and presented in **Table 19** below.

Table 19. Fast Pyrolysis and Bio-oil Upgrading Capital Costs (millions of $)

Process Section	***PID***	***Installed***	***Uninstalled***	
Feedstock Handling and Prep	A100	$ 21.4	$ 8.7	6%
Fast Pyrolysis	A100	$210.0	$ 61.9	59%
Hydrotreating	A310	$ 76.3	$ 35.6	21%
Hydrogen Plant	A400	$ 41.1	$ 21.4	11%
Utilities	A700	$ 9.2	$ 3.2	3%
Total		**$358.0**	**$130.8**	**100%**

A summary of the production cost estimate for the fast pyrolysis case is shown in **Table 20**. The costs are given for both the primary fast pyrolysis step only, as well as the additional fixed and variable costs for upgrading the bio-oil to hydrocarbon liquids. Catalyst replacement costs are indicated in the table also. The three catalysts used in the upgrading as well as a cost for the reforming catalyst for hydrogen production are included. The catalyst lifetimes are all assumed at one year. The total costs of the finished product, for both primary bio-oil production, as well as upgraded hydrocarbon liquid production, are calculated in the bottom row.

Table 20. Fast Pyrolysis production cost estimate

	Fast Pyrolysis			Upgrading		
	M $/a	$/t	$/GJ	M $/a	$/t	$/GJ
FIXED OPERATING COST						
Operating labor	1.1	3	0.2	0.3	2	0.1
Maintenance labor	2.3	6	0.4	1.3	9	0.2
Overheads	4.6	11	0.8	2.5	18	0.4
Maintenance materials	6.9	17	1.1	3.8	27	0.6
Taxes, insurance	4.6	11	0.8	2.5	18	0.4
Others	2.3	6	0.4	1.3	9	0.2
Total	21.9	52	3.6	11.7	84	2.0
CATALYST COST						
Hydrogen plant catalyst				0.2	2	0.0
Stabilizer catalyst				4.6	33	0.8
1st HDO catalyst				10.4	75	1.8
2nd HDO catalyst				4.3	31	0.7
Total				19.5	138	3.3
VARIABLE OPERATING COST						
Feedstock	35.0	84	5.8	96.7	694	16.5
Electricity	5.8	14	0.9	7.3	53	1.3
Waste water treatment	0.0	0	0.0	0.1	1	0.0
Natural gas	0.0	0	0.0	0	0	0.0
Total	40.8	98	6.7	104.2	747	17.8
CAPITAL CHARGES	34.0	81	5.6	18.6	134	3.2
PRODUCTION COST	96.7	231	16.0	153.9	1103	26.3

6.4 Hydrothermal Liquefaction and Biocrude Hydrotreating Costs

The capital costs for hydrothermal liquefaction are grouped into the subsections of the process and presented in **Table 21** below.

Table 21. Hydrothermal Liquefaction and Biocrude Hydrotreating Capital Costs (millions of $)

Process Section	***PID***	***Installed***	***Uninstalled***	
Feed Handling and Preparation	A100	$ 22.5	$ 9.8	9%
HTL Oil Production	A200	$150.8	$ 75.0	62%
Wastewater Treatment	A240	$ 22.0	$ 8.9	9%
HTL Oil Upgrading	A310	$ 21.6	$ 20.9	9%
Hydrogen Plant	A400	$ 19.5	$ 10.1	8%
Utilities	A700	$ 7.9	$ 1.0	3%
Total		**$244.3**	**$125.7**	**100%**

A summary of the production cost estimate for the hydrothermal liquefaction case is shown in **Table 22**. The costs are given for both the primary liquefaction step only, as well as the additional fixed and variable costs for hydrotreating the biocrude to hydrocarbon liquids. Catalyst replacement costs are indicated in the table also. The hydrotreating catalyst used in the upgrading as well as a cost for the reforming catalyst for hydrogen production are included. The catalyst lifetimes are both assumed at one year. The total costs of the finished product, for both primary bio-oil production, as well as upgraded hydrocarbon liquid production, are calculated in the bottom row.

Table 22. Hydrothermal Liquefaction production cost estimate

	Hydrothermal Liquefaction			Upgrading		
	M $/a	$/t	$/GJ	M $/a	$/t	$/GJ
FIXED OPERATING COST						
Operating labor	1.1	5	0.2	0.3	2	0.0
Maintenance labor	2.0	9	0.3	0.5	3	0.1
Overheads	3.9	18	0.6	1.0	6	0.1
Maintenance materials	5.9	27	0.9	1.5	9	0.2
HTL catalyst	3.4	16	0.5			
Taxes, insurance	3.9	18	0.6	1.0	6	0.1
Others	2.0	9	0.3	0.5	3	0.1
Total	22.1	103	3.3	4.7	30	0.7
CATALYST COST						
H_2 plant catalyst				0.1	1	0.0
HDO catalyst				3.9	24	0.6
Total				4.0	25	0.6
VARIABLE OPERATING COST						
Feedstock	35.0	163	5.3	96.1	600	14.2
Solids Disposal	0.6	3	0.1			
Electricity	9.2	43	1.4	1.9	12	0.3
Waste water treatment	0.5	2	0.1	0.0	0	0.0
Total	45.2	211	6.8	98.0	612	14.5
CAPITAL CHARGES	28.7	134	4.3	7.2	45	1.1
PRODUCTION COST	96.1	449	14.5	114.0	712	16.9

7.0 Discussion and Conclusions

7.1 Comparison of FP and HTL Results

The differences in the processes led to significant differences in the results related to the process yields, efficiencies, and costs as presented in **Table 23**. The energy efficiency to bio-oil/biocrude intermediate in the primary liquefaction step is essentially the same for both processes even though the FP route gives nearly twice the mass yield. The capital investment for the fast pyrolysis process is only slightly more than the hydrothermal liquefaction process. The much lower energy content of the FP bio-oil compared to the HTL biocrude causes the FP bio-oil to be more expensive on an energy basis while much cheaper on a mass basis. The HTL pathway delivers higher mass and energy efficiencies compared to FP when considering the total process to hydrocarbon liquid fuels. As a result, the HTL hydrotreated product is cheaper on both a mass basis and an energy basis. The FP upgraded product is a slightly more energy dense product (more completely hydrogenated). The more complex upgrading process, and required higher capital costs, cause it to be more expensive on both a mass and energy basis.

Table 23. Comparison of the Results for Fast Pyrolysis versus Hydrothermal Liquefaction

	FP	FP + Upgrading	HTL	HTL + HT
Energy efficiency to liquid fuel, LHV	60.2	54.4	64.5	62.3
Fixed Capital Investment, $M	231	358	195	244
Liquid fuel mass yield, % feed, dry basis	51.1	24.2	35.1	27.4
Liquid fuel product cost, $/GJ	16.0	26.3	14.5	16.9
Liquid fuel product cost, $/metric ton	231	1103	449	712
Liquid fuel product cost, $/gallon gasoline equivalent	NA	3.09	NA	2.00

7.2 Comparison with the IEA DBL Results

The initial intention of this study was to update the earlier technoeconomic comparative assessment undertaken in the 1980s by the IEA Bioenergy Direct Biomass Liquefaction team[4] based on the process developments over the past quarter century and in light of the changes in strategy for hydrothermal liquefaction and fast pyrolysis bio-oil upgrading. Since that study, hydrothermal liquefaction has been simplified by the removal of the reducing gas atmosphere and the focus on once through processing of biomass in an aqueous slurry. Similarly, the difficulties in upgrading of fast pyrolysis bio-oil have been further investigated and have led to additional low-temperature catalytic processing to stabilize the bio-oil prior to higher temperature catalytic hydrotreating and hydrocracking.

In **Table 24** a comparison is made of the process results from the IEA study[1] and the current study. For comparison we have used the IEA fast pyrolysis (AFP) potential case, which was based on a case that was only conceptual at that time of a circulating fluid-bed pyrolysis system, and the liquefaction (LIPS) present case, which used the lower concentration slurries more aligned with the water slurry feedstock modeled in the current study. It is clear that the simplification of HTL, by eliminating the reducing gas production and processing environment has improved its relative standing compared to fast pyrolysis. While the overall efficiency and yields were lower and the costs were higher for HTL in the earlier study, these new results suggest that the process can be even more efficient and less costly than fast pyrolysis. The comparison of the capital costs has shifted such that those of the high-pressure HTL process are about the same as for FP for the liquefaction step while the hydrotreating capital cost for HTL is less than the upgrading of fast pyrolysis bio-oil. Compared to the earlier study wherein the capital cost for the HTL process was 1.9 times the FP process, in the current study the capital for FP is 1.5 times that for HTL. The overall mass yield of product calculated for HTL is slightly higher than FP, compared to being slightly lower in the earlier study. Although the product costs are higher than in the earlier study, when compared to the current costs of equivalent products, the FP upgraded product has dropped slightly in relative cost, while the relative cost of the HTL hydrotreated product has dropped dramatically from 2.0 to 0.8. Part of this drop in relative cost in both cases can be attributed to the use of lower cost forest residue biomass as a feedstock. The current study is based on $30 per wet ton while the earlier work used $30 per dry ton (considered high for the U.S. at that time).

Table 24. Comparison of the Results of the IEA DBL Study with the Current Effort

	IEA DBL Process Models[1]		Current Study	
	AFP Potential	LIPS Present	FP & Upgrade	HTL & HT
Total energy efficiency to product, LHV	52	41	50	57
Fixed Capital Investment, $M	AFP	AFP x 1.9	358	244
Product mass yield, % dry feed	25	23	24	27
Ratio of Product cost to value	1.2	2.0	1.2*	0.8*

Product in all cases is a mixed gasoline/diesel/heavy hydrocarbon product
Total energy efficiency assuming 40% conversion efficiency for MWth → MWe
* The equivalent values of the upgraded products for the present study were calculated on a weight averaged basis using the following values for products: gasoline = $986/ton, diesel = $916/ton, heavy hydrocarbon product = $698/ton. The weight averaged total product value for upgraded FP is $925/ton and for hydrotreated HTL the total product value is $915/ton.

7.3 Uncertainties Needing Further Research for FP

The FP model assumes that there is no ash left in the bio-oil and that it is all removed from the system in the char. In fact, the separation is not perfect and there is certainly some mineral content left in the bio-oil. Mineral deposition in the catalytic hydrotreater could be an issue in long-term operation. The effects of long-term operation could be significant without sufficient flushing of mineral content from the catalyst bed by the water.

The FP model includes a multi-stage hydroprocessing reactor system which has only been developed to laboratory bench-scale. The use of a precious metal catalyst in the first stage of the hydroprocessing is considered problematic. Longer-term operations of up to 1440 h have demonstrated that the multi-stage concept can be made to work, if proper first stage stabilization is accomplished.

Use of the aqueous byproducts from hydrotreating and steam reforming for makeup water in the steam generator for hydrogen production needs to be demonstrated. The quality of the aqueous products was assumed to be sufficient and the fouling by the trace hydrocarbon organics was considered unimportant.

Direct steam reforming of the byproduct gases from the pyrolysis unit as well as the hydrotreater systems was also assumed. Although limited studies have confirmed that the pyrolysis gases can be directly reformed, the direct reforming of the hydrocarbon-containing gas product from the bio-oil upgrader has not been tested at any scale.

Further research on the composition of primary bio-oil is needed in order to better represent families of compounds using Aspen Plus® database model compounds. Although a significant effort was made within this study to accurately depict all primary and upgraded products, the largest effort was on identifying appropriately representative upgraded product compounds. However, the use of Aspen-Plus software in the fractionation of the product components was not uniformly representative of the gasoline and diesel product groups as shown by the difference in the model compositions for these product groups, which then reflected on the energy efficiency calculations. Bio-oil compounds are more challenging as analysis of such oxygenated oils is difficult using standard methods such as GCMS. NMR data helped to inform some of the model compound choices, but further investigation would help enhance the accuracy of representing major product groups.

The overall energy balance for the fast pyrolysis process is off by 3.9%. This is largely related to the hydroprocessing product specification and the choice of model components for this part of the model. The energy balance for other individual blocks range within a window of 0.04 – 0.5%. Further model development may allow these parameters to be tightened up.

7.4 Uncertainties Needing Further Research for HTL

The HTL model is based on 8% solids in the water slurry. This is a conservative assumption which requires larger volume in the high-pressure reactor and drives up water recycle and associated heat losses. Pumping to high-pressure for hydrothermal processing of slurries at 8% biomass solids in water is relatively straightforward. Laboratory processing of wood in water slurries at up to 13 wt% have been demonstrated with sufficient wet milling of the biomass. The scale-up and cost of such a pretreatment is an important area of further research.

Further, the Case D from the Harris report was used for the reactor concept and that configuration requires the demonstration of a high-temperature liquid-phase separator, which would allow the recycle of the hot water to the slurry formation and facilitate heat integration.

The HTL model assumes that there is no ash left in the biocrude or the aqueous byproduct and that it is all removed from the system in the solids separator. In fact, the separation is not perfect and there is certainly some mineral content left in both the aqueous and biocrude products. The effects of long-term operation could be significant without sufficient flushing of mineral content from the water via the wastewater stream to Anaerobic Digestion. Further, mineral deposition in the catalytic hydrotreater could be an issue in long-term operation.

While in the model the aqueous byproduct is sent to anaerobic digestion for recovery of the dissolved organic as methane gas for hydrogen production, the biological treatment of such water has not been demonstrated. The alternative of catalytic hydrothermal gasification may be a better option, but its higher risk and developmental uncertainty call for more testing.

The use of the aqueous byproducts from hydrotreating and steam reforming for makeup water in the steam generator for hydrogen production needs to be demonstrated also. The quality of the aqueous products was assumed to be sufficient and the potential for fouling by the trace hydrocarbon organics was considered unimportant.

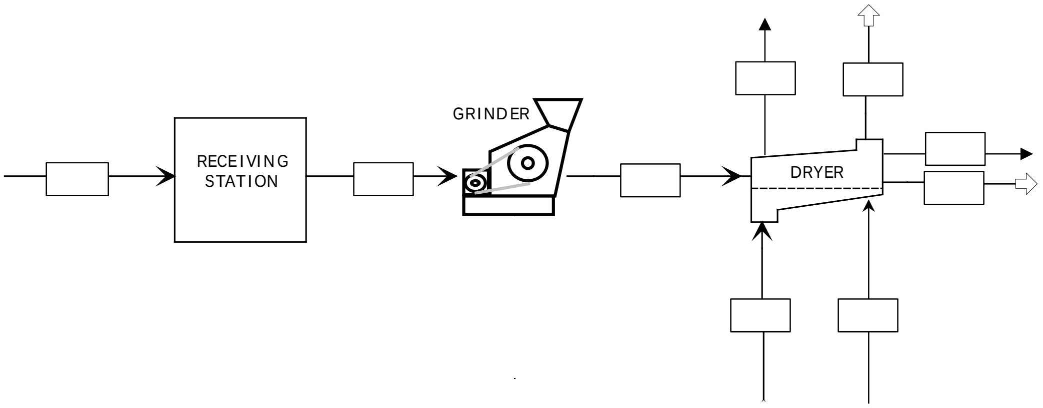
Direct steam reforming of the hydrotreater product gases and the anaerobic digestion gas was assumed. The direct reforming of the hydrocarbon-containing gas product from the biocrude hydrotreater has not been tested at any scale. Reforming of AD gas also needs to be validated and any gas processing requirements determined.

Further research on the composition of primary biocrude is needed in order to better represent families of compounds using Aspen Plus® database model compounds. Although a significant effort was made within this study to accurately depict all primary and upgraded products, the largest effort was on identifying correct upgraded product compounds. However, the use of Aspen-Plus software in the fractionation of the product components was not uniformly representative of the gasoline and diesel product groups as shown by the difference in the model compositions for these product groups, which then reflected on the energy efficiency calculations. Biocrude compounds are more challenging as analysis of such oxygenated oils is difficult using standard methods such as GCMS. NMR data helped to inform some of the model compound choices, but further investigation would help enhance the accuracy of representing major product groups.

8.0 Appendix

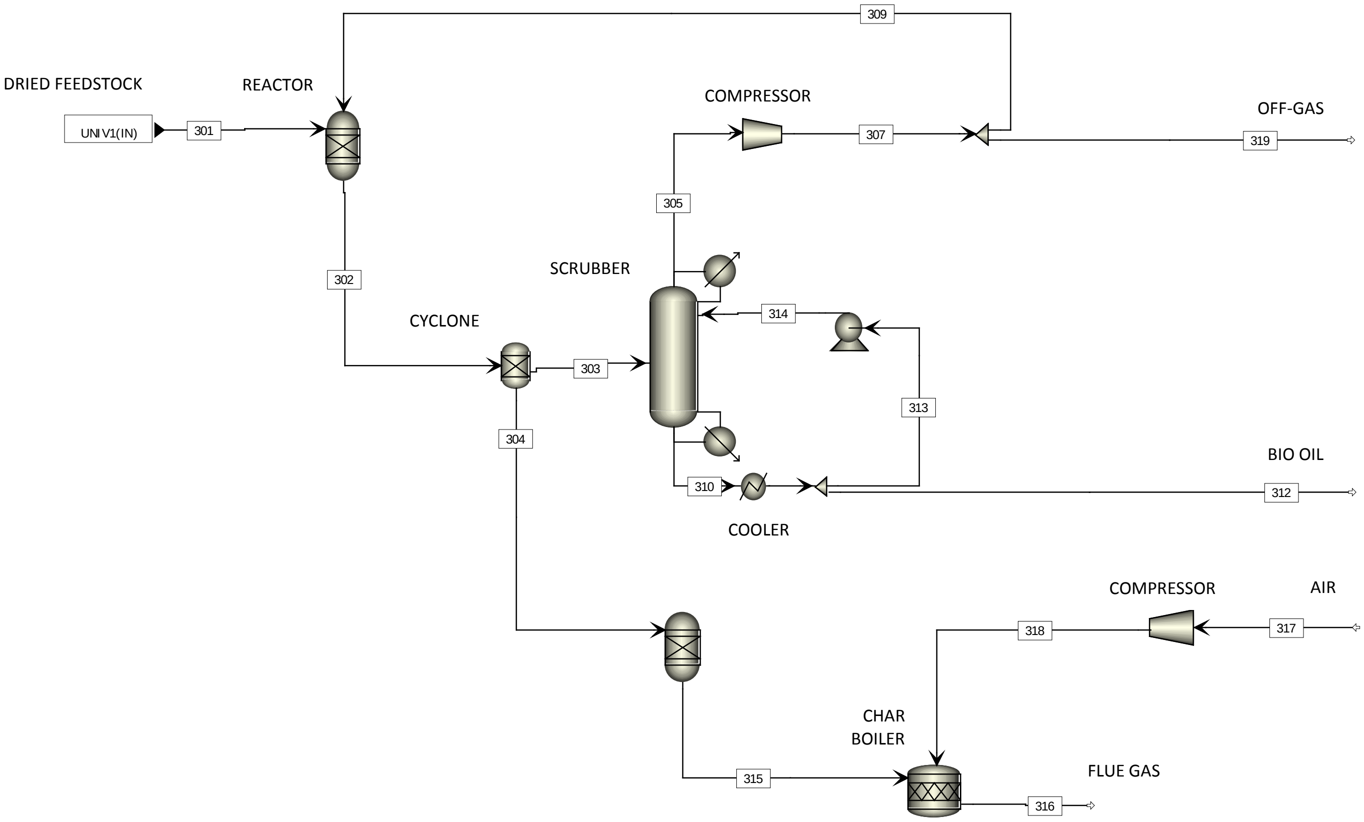
The following sections provide the process diagrams and the data tables from the Aspen Plus® modeling of fast pyrolysis and bio-oil upgrading and hydrothermal liquefaction and biocrude hydrotreating. Note: Quantities in stream tables are for one train of 500 tDM/day

8.1 FP pre-treatment



Stream no.	100	101	102	103	104	105	106	107	108
Temperature C	25	25	25	25	0	25	25	127,4	120,3
Pressure bar	1	1	1	1	1,01325	1	1	2	2
Vapor Frac	0	0	0	0	1	1	0	1	0,8990334
Total Flow cu	5,82E-03	5,82E-03	5,82E-03	5,06E-04	198,6225	207,2067	5,32E-03	12,81183	11,31485
Enthalpy J/k	-2,86E+08	-2,86E+08	-2,86E+08	-2,86E+08	-3,94E+05	-3,50E+04	-2,86E+08	-238350000	-2,43E+08
Total Flow kg/	20835	20835	20835	1811,739	947 326,00	947 326,00	19023,26	49900	49900
H2O	20835	20835	20835	1811,739	0	0	19023,26	49900	49900
N2	0	0	0	0	748 387,00	748 387,00	0	0	0
O2	0	0	0	0	198 938,00	198 938,00	0	0	0
Total Flow kg/	41670	41670	41670	22646,74	947 326,00	947 326,00	19023,26	49900	49900
Substream: NC									
Mass Flow kg									
WOOD	20835	20835	20835	20835	0	0	0	0	0

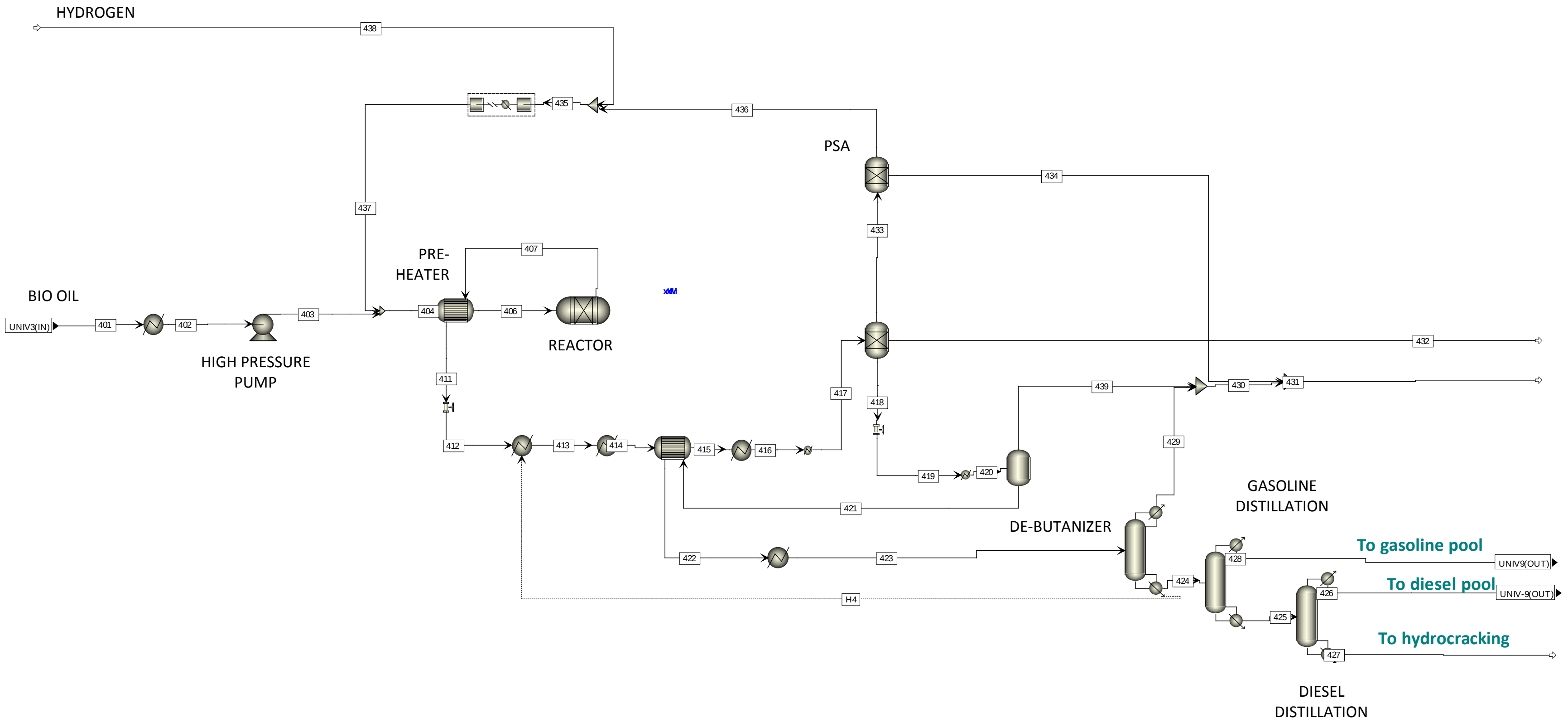
8.2 Fast Pyrolysis



	301	302	303	304	305	307	309	310	312	313	314	315	316	317	318	319
Temperature C	40	520	520		40	65,94556	66,5525	60,81175	35	35	35,12746	480	1341,287	25	37,52781	66,5525
Pressure bar	1,01325	1,01325	1,01325	1,01325	1,01325	1,2	1,2	1,01325	1,01325	1,01325	3	1,01325	1,01325	1,01325	1,09	1,2
Total Flow cum/sec	5,14E-04	7,381634	7,369977	0	9,305353	8,508202	7,968344	0,1904098	3,32E-03	0,1823651	0,1823872	1,510701	72,87562	12,99373	12,5877	0,5415748
Enthalpy J/kmol	-2,85E+08	-2,50E+08			-1,97E+08	-1,96E+08	-1,96E+08	-3,58E+08	-3,61E+08	-3,61E+08	-3,61E+08	1,37E+07	-2,63E+07	-6531,045	3,59E+05	-1,96E+08
Total Flow kg/hr	**22646,74**	**22646,74**	**17569,7649**	**5076,974**	**40570,77**	**40570,77**	**37988,83**	**8,38E+05**	**14988,61**	**8,23E+05**	**8,23E+05**	**5076,974**	**60494,31**	**55000**	**55000**	**2581,941**
C2H4O-01	0	403,4964	403,4964	0	79,6919	79,6919	74,62027	22287,8	398,4162	21889,39	21889,39	0	0	0	0	5,071626
C2H6O-01	0	19,21411	19,21411	0	0,0136091	0,0136091	0,012743	1074,895	19,21479	1055,68	1055,68	0	0	0	0	8,66E-04
C3H6O-01	0	432,3176	432,3176	0	14,23302	14,23302	13,32723	24134,57	431,429	23703,14	23703,14	0	0	0	0	0,9057955
C2H4O-02	0	1296,953	1296,953	0	18,17706	18,17706	17,02026	72492,53	1295,875	71196,66	71196,66	0	0	0	0	1,156796
C7H8O-01	0	1702,37	1702,37	0	1,976963	1,976963	1,851148	95227,71	1702,288	93525,42	93525,42	0	0	0	0	0,1258148
C5H4O-01	0	401,575	401,575	0	38,77365	38,77365	36,30607	22327,48	399,1256	21928,36	21928,36	0	0	0	0	2,467571
LEVOGLUC	0	4114,062	4114,062	0	2,51E-07	2,51E-07	2,35E-07	2,30E+05	4114,336	2,26E+05	2,26E+05	0	0	0	0	1,60E-08
CO2	0	1196,893	1196,893	0	18336,39	18336,39	17169,46	1677,977	29,99547	1647,981	1647,981	0	14456,8	0	0	1166,936
CH4	0	162,1525	162,1525	0	2542,921	2542,921	2381,088	17,72398	0,3168334	17,40714	17,40714	0	0	0	0	161,8325
H2O	1811,739	4381,867	4381,867	0	1524,35	1524,35	1427,34	2,40E+05	4285,122	2,35E+05	2,35E+05	0	1210,871	0	0	97,01026
N2	0	0	0	0	1,06E-03	1,06E-03	9,94E-04	1,63E-05	2,91E-07	1,60E-05	1,60E-05	12,501	43462,5	43450	43450	6,76E-05
CO	0	1007,404	1007,404	0	15749,84	15749,84	14747,51	283,1287	5,061201	278,0675	278,0675	0	0	0	0	1002,326
H2	0	0	0	0	0	0	0	0	0	0	0	123,2526	0	0	0	0
O2	0	0	0	0	0	0	0	0	0	0	0	843,1064	1049,103	11550	11550	0
NO	0	0	0	0	0	0	0	0	0	0	0	0	2,50E-04	0	0	0
S	0	0	0	0	0	0	0	0	0	0	0	1,2501	0	0	0	0
C2H6-02	0	35,3407	35,3407	0	552,2624	552,2624	517,1162	10,8462	0,1938864	10,65232	10,65232	0	0	0	0	35,14621
C2H4-02	0	109,6413	109,6413	0	1711,89	1711,89	1602,945	38,84392	0,6943729	38,14954	38,14954	0	0	0	0	108,9454
SO2	0	0	0	0	0	0	0	0	0	0	0	0	2,504319	0	0	0
C18H3-01	0	1276,778	1276,778	0	0,0567176	0,0567176	0,053108	71431,17	1276,902	70154,27	70154,27	0	0	0	0	3,61E-03
C4H10-01	0	16,55941	16,55941	0	0,1755143	0,1755143	0,1643445	925,6936	16,54768	909,1459	909,1459	0	0	0	0	0,0111698
C4H7N-01	0	303,8199	303,8199	0	0,0111301	0,0111301	0,0104218	16995,13	303,8045	16691,32	16691,32	0	0	0	0	7,08E-04
PYROLIGN	0	709,321	709,321	0	6,43E-15	6,43E-15	6,02E-15	39678,21	709,2866	38968,92	38968,92	0	0	0	0	4,09E-16
Total Flow kg/hr	1811,739	17569,76	17569,769	0	40570,77	40570,77	37988,83	8,38E+05	14988,61	8,23E+05	8,23E+05	980,1101	60181,78	55000	55000	2581,941
Substream: CISOLID																
Mass Flow kg/hr																
C	0	0	0	0	0	0	0	0	0	0	0	3784,339	0	0	0	0
Substream: NC																
Mass Flow kg/hr																
CHAR	0	4764,449	0	4764,449	0	0	0	0	0	0	0	0	0	0	0	0
ASH	0	312,525	0	312,525	0	0	0	0	0	0	0	312,525	312,525	0	0	0

Note: Stream tables are for one train (out of four) of 500 tDM/day

8.3 Fast pyrolysis bio-oil upgrading

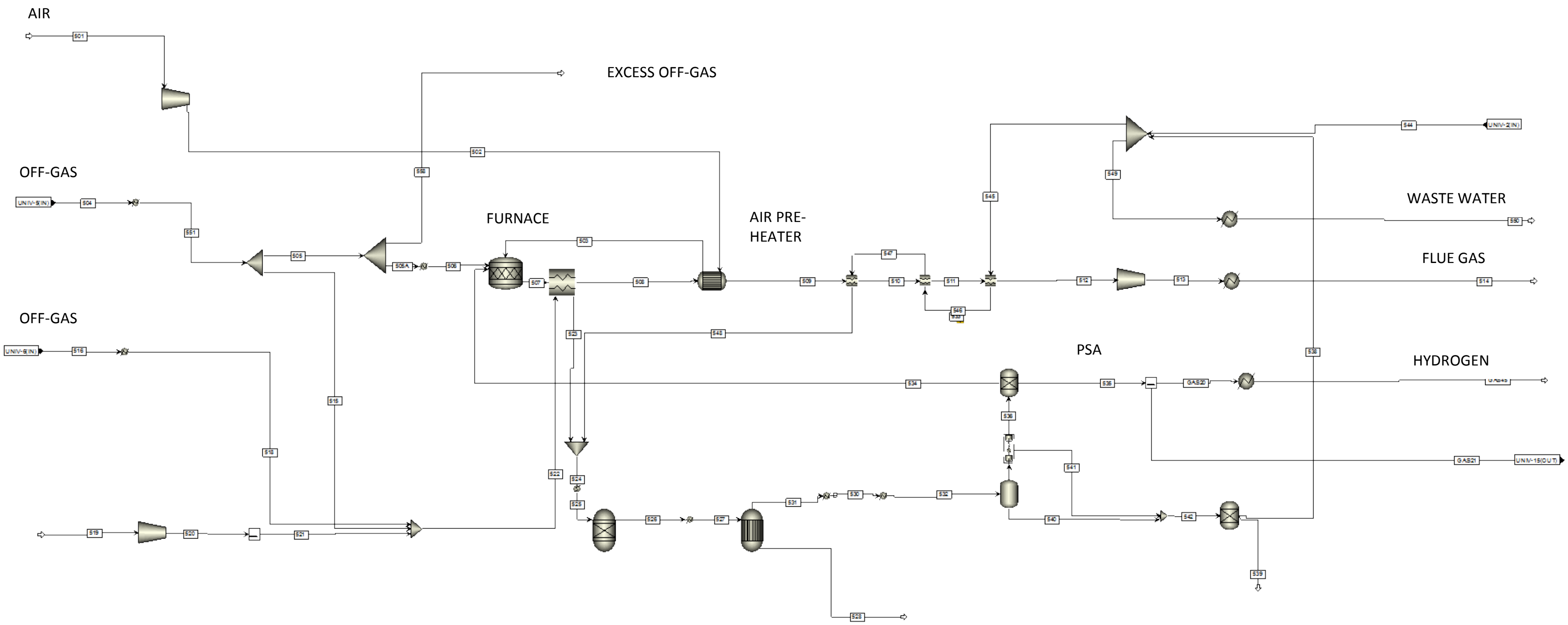


	401	402	403	404	406	407	411	412	413	414	415	416	417	418	419	420	421	422
Temperature C	35,00	35,00	42,83	81,39	165,56	433,36	301,10	263,83	250,07	132,22	127,12	60,00	43,33	43,33	46,03	46,03	46,03	93,33
Pressure bar	1,01	1,01	137,41	137,27	136,93	136,24	136,21	49,99	49,92	49,88	49,88	49,74	49,39	49,39	3,79	3,79	3,79	3,72
Vapor Frac	0,00	0,00	0,00	0,64	0,68	1,00	1,00	0,98	1,00	0,51	0,51	0,48	0,48	0,00	0,00	0,00	0,00	0,00
Total Flow cum/sec	0,00	0,00	0,00	0,04	0,05	0,10	0,07	0,21	0,19	0,08	0,08	0,06	0,06	0,00	0,00	0,00	0,00	0,00
Enthalpy J/kmol	-360 810 000	-359 140 000	-358 430 000	-130 990 000	-123 580 000	-130 100 000	-137 900 000	-137 900 000	-139 100 000	-163 530 000	-164 110 000	-170 060 000	-171 280 000	-145 980 000	-145 980 000	-145 980 000	-145 980 000	-134 110 000
Mass Flow kg/hr	**14 952,35**	**14 952,35**	**14 952,35**	**16 083,07**	**16 083,07**	**16 083,07**	**16 083,07**	**16 083,07**	**16 083,07**	**16 083,07**	**16 083,07**	**16 083,07**	**16 083,07**	**5 152,05**	**5 152,05**	**5 152,05**	**5 152,05**	**5 152,05**
C2H4O-01	398,42	398,42	398,42	398,42	398,42	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
C2H6O-01	19,21	19,21	19,21	19,21	19,21	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
C3H6O-01	431,43	431,43	431,43	431,43	431,43	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
C2H4O-02	1 295,88	1 295,88	1 295,88	1 295,88	1 295,88	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
C7H8O-01	1 702,29	1 702,29	1 702,29	1 702,29	1 702,29	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
C5H4O-01	399,13	399,13	399,13	399,13	399,13	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
LEVOGLUC	4 114,34	4 114,34	4 114,34	4 114,34	4 114,34	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
CO2	0,00	0,00	0,00	0,00	0,00	1 007,65	1 007,65	1 007,65	1 007,65	1 007,65	1 007,65	1 007,65	1 007,65	0,00	0,00	0,00	0,00	0,00
CH4	0,00	0,00	0,00	0,00	0,00	480,44	480,44	480,44	480,44	480,44	480,44	480,44	480,44	0,00	0,00	0,00	0,00	0,00
H2O	4 285,12	4 285,12	4 285,12	4 285,12	4 285,12	7 933,24	7 933,24	7 933,24	7 933,24	7 933,24	7 933,24	7 933,24	7 933,24	0,00	0,00	0,00	0,00	0,00
CO	0,00	0,00	0,00	0,00	0,00	51,04	51,04	51,04	51,04	51,04	51,04	51,04	51,04	0,00	0,00	0,00	0,00	0,00
H2	0,00	0,00	0,00	1 130,73	1 130,73	565,37	565,37	565,37	565,37	565,37	565,37	565,37	565,37	0,00	0,00	0,00	0,00	0,00
NH3	0,00	0,00	0,00	0,00	0,00	60,80	60,80	60,80	60,80	60,80	60,80	60,80	60,80	0,00	0,00	0,00	0,00	0,00
C2H6-02	0,00	0,00	0,00	0,00	0,00	402,61	402,61	402,61	402,61	402,61	402,61	402,61	402,61	0,00	0,00	0,00	0,00	0,00
C18H3-01	1 276,90	1 276,90	1 276,90	1 276,90	1 276,90	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
C4H10-01	16,55	16,55	16,55	16,55	16,55	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
C4H7N-01	303,80	303,80	303,80	303,80	303,80	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
PYROLIGN	709,29	709,29	709,29	709,29	709,29	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
N-HEX-01	0,00	0,00	0,00	0,00	0,00	505,41	505,41	505,41	505,41	505,41	505,41	505,41	505,41	505,41	505,41	505,41	505,41	505,41
N-DOD-01	0,00	0,00	0,00	0,00	0,00	538,89	538,89	538,89	538,89	538,89	538,89	538,89	538,89	538,89	538,89	538,89	538,89	538,89
4-MET-01	0,00	0,00	0,00	0,00	0,00	546,37	546,37	546,37	546,37	546,37	546,37	546,37	546,37	546,37	546,37	546,37	546,37	546,37
ETHYL-01	0,00	0,00	0,00	0,00	0,00	523,29	523,29	523,29	523,29	523,29	523,29	523,29	523,29	523,29	523,29	523,29	523,29	523,29
1-MET-01	0,00	0,00	0,00	0,00	0,00	314,58	314,58	314,58	314,58	314,58	314,58	314,58	314,58	314,58	314,58	314,58	314,58	314,58
CYCLO-01	0,00	0,00	0,00	0,00	0,00	313,67	313,67	313,67	313,67	313,67	313,67	313,67	313,67	313,67	313,67	313,67	313,67	313,67
N-PRO-01	0,00	0,00	0,00	0,00	0,00	173,33	173,33	173,33	173,33	173,33	173,33	173,33	173,33	173,33	173,33	173,33	173,33	173,33
1:3-D-01	0,00	0,00	0,00	0,00	0,00	155,41	155,41	155,41	155,41	155,41	155,41	155,41	155,41	155,41	155,41	155,41	155,41	155,41
4-MET-02	0,00	0,00	0,00	0,00	0,00	209,44	209,44	209,44	209,44	209,44	209,44	209,44	209,44	209,44	209,44	209,44	209,44	209,44
INDAN-01	0,00	0,00	0,00	0,00	0,00	175,58	175,58	175,58	175,58	175,58	175,58	175,58	175,58	175,58	175,58	175,58	175,58	175,58
1-N-H-01	0,00	0,00	0,00	0,00	0,00	285,92	285,92	285,92	285,92	285,92	285,92	285,92	285,92	285,92	285,92	285,92	285,92	285,92
PROPA-01	0,00	0,00	0,00	0,00	0,00	248,05	248,05	248,05	248,05	248,05	248,05	248,05	248,05	0,00	0,00	0,00	0,00	0,00
N-BUT-01	0,00	0,00	0,00	0,00	0,00	248,66	248,66	248,66	248,66	248,66	248,66	248,66	248,66	163,61	163,61	163,61	163,61	163,61
N-PEN-01	0,00	0,00	0,00	0,00	0,00	91,46	91,46	91,46	91,46	91,46	91,46	91,46	91,46	0,00	0,00	0,00	0,00	0,00
HYDRO-03	0,00	0,00	0,00	0,00	0,00	5,31	5,31	5,31	5,31	5,31	5,31	5,31	5,31	0,00	0,00	0,00	0,00	0,00
THYMO-01	0,00	0,00	0,00	0,00	0,00	200,00	200,00	200,00	200,00	200,00	200,00	200,00	200,00	200,00	200,00	200,00	200,00	200,00
P-ETH-01	0,00	0,00	0,00	0,00	0,00	354,48	354,48	354,48	354,48	354,48	354,48	354,48	354,48	354,48	354,48	354,48	354,48	354,48
1:2-D-01	0,00	0,00	0,00	0,00	0,00	367,17	367,17	367,17	367,17	367,17	367,17	367,17	367,17	367,17	367,17	367,17	367,17	367,17
1-PHE-01	0,00	0,00	0,00	0,00	0,00	87,10	87,10	87,10	87,10	87,10	87,10	87,10	87,10	87,10	87,10	87,10	87,10	87,10
O-PHE-01	0,00	0,00	0,00	0,00	0,00	237,80	237,80	237,80	237,80	237,80	237,80	237,80	237,80	237,80	237,80	237,80	237,80	237,80
Total Flow kg/hr	14 952,35	14 952,35	14 952,35	16 083,07	16 083,07	16 083,07	16 083,07	16 083,07	16 083,07	16 083,07	16 083,07	16 083,07	16 083,07	5 152,05	5 152,05	5 152,05	5 152,05	5 152,05

	423	424	425	426	427	428	429	430	431	432	433	434	435	436	437	438	439
Temperature C	93,33	166,07	249,98	226,33	320,04	105,74	48,97	48,97	29,06	43,33	43,33	43,33	41,62	43,33	60	40	
Pressure bar	3,72	3,45	1,36	1,08	1,08	1,36	3,31	3,31	3,31	49,39	49,39	49,39	20,00	21,70	137,27	20	3,79
Vapor Frac	0,00	0,00	0,00	0,00	0,00	0,00	1,00	1,00	1,00	0,00	1,00	1,00	1,00	1,00	1	1	
Total Flow cum/sec	0,00	0,00	0,00	0,00	0,00	0,00	0,01	0,01	0,29	0,00	0,05	0,02	0,20	0,08	0,03	0,12	0
Enthalpy J/kmol	-134 110 000	-112 260 000	-16 803 000	-100 800 000	202 913 000	-153 340 000	-126 260 000	-126 260 000	-100 930 000	-286 700 000	-37 454 000	-100 430 000	479 119	549 307	1 010 750	432 327	
Mass Flow kg/hr	**5 152,05**	**4 990,40**	**2 116,02**	**1 424,27**	**691,75**	**2 874,38**	**161,65**	**161,65**	**2 707,14**	**7 933,24**	**2 997,78**	**2 545,49**	**1 130,73**	**452,29**	**1130,73**	**678,43**	**0**
C2H4O-01	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0	0	0
C2H6O-01	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0	0	0
C3H6O-01	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0	0	0
C2H4O-02	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0	0	0
C7H8O-01	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0	0	0
C5H4O-01	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0	0	0
LEVOGLUC	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0	0	0
CO2	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	1 007,65	0,00	1 007,65	1 007,65	0,00	0,00	0	0	0
CH4	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	480,44	0,00	480,44	480,44	0,00	0,00	0	0	0
H2O	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	7 933,24	0,00	0,00	0,00	0,00	0	0	0
CO	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	51,04	0,00	51,04	51,04	0,00	0,00	0	0	0
H2	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	113,07	0,00	565,37	113,07	1 130,73	452,29	1130,73	678,43	0
NH3	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	60,80	0,00	60,80	60,80	0,00	0,00	0	0	0
C2H6-02	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	402,61	0,00	402,61	402,61	0,00	0,00	0	0	0
C18H3-01	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0	0	0
C4H10-01	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0	0	0
C4H7N-01	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0	0	0
PYROLIGN	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0	0	0
N-HEX-01	505,41	491,97	0,00	0,00	0,00	491,97	13,44	13,44	13,44	0,00	0,00	0,00	0,00	0,00	0	0	0
N-DOD-01	538,89	538,89	533,25	532,82	0,43	5,64	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0	0	0
4-MET-01	546,37	546,37	0,01	0,01	0,00	546,36	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0	0	0
ETHYL-01	523,29	523,29	0,00	0,00	0,00	523,29	0,01	0,01	0,01	0,00	0,00	0,00	0,00	0,00	0	0	0
1-MET-01	314,58	314,58	0,00	0,00	0,00	314,58	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0	0	0
CYCLO-01	313,67	312,71	0,00	0,00	0,00	312,71	0,96	0,96	0,96	0,00	0,00	0,00	0,00	0,00	0	0	0
N-PRO-01	173,33	173,33	0,00	0,00	0,00	173,33	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0	0	0
1:3-D-01	155,41	155,41	124,33	124,19	0,14	31,08	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0	0	0
4-MET-02	209,44	209,44	209,44	1,17	208,27	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0	0	0
INDAN-01	175,58	175,58	0,11	0,11	0,00	175,47	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0	0	0
1-N-H-01	285,92	285,92	285,92	97,58	188,34	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0	0	0
PROPA-01	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	248,05	0,00	248,05	248,05	0,00	0,00	0	0	0
N-BUT-01	163,61	16,36	0,00	0,00	0,00	16,36	147,25	147,25	232,30	0,00	85,06	85,06	0,00	0,00	0	0	0
N-PEN-01	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	91,46	0,00	91,46	91,46	0,00	0,00	0	0	0
HYDRO-03	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	5,31	0,00	5,31	5,31	0,00	0,00	0	0	0
THYMO-01	200,00	200,00	200,00	199,58	0,42	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0	0	0
P-ETH-01	354,48	354,48	70,90	70,87	0,03	283,58	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0	0	0
1:2-D-01	367,17	367,17	367,17	306,21	60,95	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0	0	0
1-PHE-01	87,10	87,10	87,10	3,20	83,91	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0	0	0
O-PHE-01	237,80	237,80	237,80	88,54	149,27	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0	0	0
Total Flow kg/hr	5 152,05	4 990,40	2 116,02	1 424,27	691,75	2 874,38	161,65	161,65	2 707,14	7 933,24	2 997,78	2 545,49	1 130,73	452,29	1130,73	678,43	0

Note: Stream tables are for one train of 500 tDM/day

8.4 Hydrogen plant

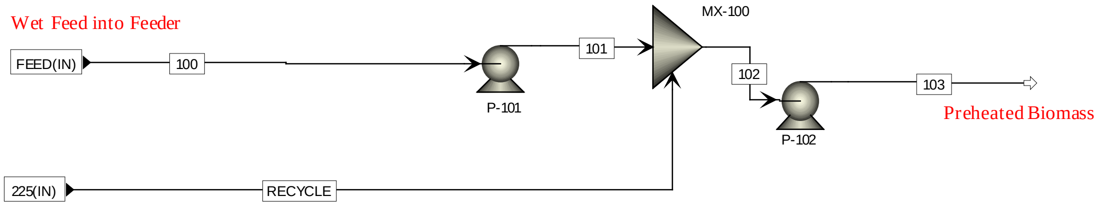


	501	502	503	504	505	505A	506	507	508	509	510	511	512	513	514	515	516	518	519	520	521	522	523	524	525
Temperature C	25	33,74232	204,4444	65,59054	65,59054	65,59054	260	900	824,235	731,6268	646,4586	179,1902	101,8476	112,6949	25	65,59054	29,056	29,056	25	25	25	37,52541	320	317,0853	847,356
Pressure bar	1,01325	1,09	0,9521049	1,01325	1,01325	1,01325	1,006355	0,9521049	0,9521049	0,9452101	0,9452101	0,9452101	0,9452101	1,02	1	1,01325	3,309483	3,309483	1,01325	1,01325	1,01325	1,01325	1,01325	0,8936399	0,8936399
Vapor Frac	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0,894028	1	1	1				1	1	1	1
Total Flow cum/sec	3,8975	3,729558	6,647841	0,646539	0,2390322	0,1381606	0,2192927	22,41096	20,96387	19,33498	17,69625	8,700443	7,214086	6,87388	4,84136	0,4065202	0,2915681	0,2915681	0	0	0	1,355105	2,591831	7,874076	14,96303
Enthalpy J/kmol	-6686,954	248345	5274210	-197150000	-197170000	-197170000	-189860000	-95338000	-98382000	-102040000	-105350000	-122200000	-124750000	-124410000	-132170000	-197170000	-100930000	-100930000				-127410000	-114910000	-188430000	-163820000
Mass Flow kg/hr	16500	16500	16500	2608,458	965,8483	558,2603	558,2603	24224,03	24224,03	24224,03	24224,03	24224,03	24224,03	24224,03	24224,03	1642,61	2707,139	2707,139	0	0	0	4349,749	4349,749	10204,72	10204,72
CO2	0	0	0	1196,931	443,1944	256,1663	256,1663	8451,775	8,45E+03	8451,775	8451,775	8451,775	8451,775	8451,775	8451,775	753,737	1007,652	1007,652	0	0	0	1761,389	1761,389	1761,389	1761,389
CH4	0	0	0	162,1494	60,03994	34,70309	34,70309	0	0	0	0	0	0	0	0	102,1094	480,4384	480,4384	0	0	0	582,5479	582,5479	582,5479	582,5479
H2O	0	0	0	97,01026	35,92052	20,76206	20,76206	1828,972	1828,972	1828,972	1828,972	1828,972	1828,972	1828,972	1828,972	61,08974	0	0	0	0	0	61,08974	61,08974	5916,056	5916,056
N2	1,30E+04	1,30E+04	1,30E+04	6,79E-05	2,51E-05	1,45E-05	1,45E-05	1,31E+04	13084,95	13084,95	13084,95	13084,95	13084,95	13084,95	13084,95	4,27E-05	0,00E+00	0,00E+00	0	0	0	4,27E-05	4,27E-05	4,27E-05	4,27E-05
CO	0	0	0	1007,388	373,0109	215,6003	215,6003	0	0	0	0	0	0	0	0	634,3766	51,04017	51,04017	0	0	0	685,4168	685,4168	685,4168	685,4168
H2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	113,0737	113,0737	0	0	0	113,0737	113,0737	113,0737	113,0737
O2	3465	3465	3465	0,00E+00	0,00E+00	0,00E+00	0,00E+00	8,48E+02	848,2347	848,2347	848,2347	848,2347	848,2347	848,2347	848,2347	0	0,00E+00	0,00E+00	0	0	0	0	0,00E+00	0,00E+00	0,00E+00
NO	0	0	0	0	0	0	0	0,1221147	0,1221147	0,1221147	0,1221147	0,1221147	0,1221147	0,1221147	0,1221147	0	0	0	0	0	0	0	0	0	0
C2H6-02	0	0	0	35,34009	13,08557	7,56346	7,56346	0	0	0	0	0	0	0	0	22,25452	402,6082	402,6082	0	0	0	424,8628	424,8628	424,8628	424,8628
C2H4-02	0	0	0	109,6398	40,59693	23,46503	23,46503	0	0	0	0	0	0	0	0	69,04287	0	0	0	0	0	69,04287	69,04287	69,04287	69,04287
SO2	0	0	0	0	0	0	0	9,980419	9,980419	9,980419	9,980419	9,980419	9,980419	9,980419	9,980419	0	0	0	0	0	0	0	0	0	0
N-HEX-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	13,43586	13,43586	0	0	0	13,43586	13,43586	13,43586	13,43586
N-DOD-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2,71E-16	2,71E-16	0	0	0	2,71E-16	2,71E-16	2,71E-16	2,71E-16
4-MET-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	7,80E-10	7,80E-10	0	0	0	7,80E-10	7,80E-10	7,80E-10	7,80E-10
ETHYL-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	7,50E-03	7,50E-03	0	0	0	7,50E-03	7,50E-03	7,50E-03	7,50E-03
1-MET-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	4,82E-05	4,82E-05	0	0	0	4,82E-05	4,82E-05	4,82E-05	4,82E-05
CYCLO-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0,963757	0,963757	0	0	0	0,963757	0,963757	0,963757	0,963757
N-PRO-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1,40E-08	1,40E-08	0	0	0	1,40E-08	1,40E-08	1,40E-08	1,40E-08
1:3-D-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2,09E-13	2,09E-13	0	0	0	2,09E-13	2,09E-13	2,09E-13	2,09E-13
4-MET-02	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2,29E-31	2,29E-31	0	0	0	2,29E-31	2,29E-31	2,29E-31	2,29E-31
INDAN-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3,70E-10	3,70E-10	0	0	0	3,70E-10	3,70E-10	3,70E-10	3,70E-10
1-N-H-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2,65E-28	2,65E-28	0	0	0	2,65E-28	2,65E-28	2,65E-28	2,65E-28
PROPA-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	248,0451	248,0451	0	0	0	248,0451	248,0451	248,0451	248,0451
N-BUT-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	232,3035	232,3035	0	0	0	232,3035	232,3035	232,3035	232,3035
N-PEN-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	91,45897	91,45897	0	0	0	91,45897	91,45897	91,45897	91,45897
HYDRO-03	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	5,311373	5,311373	0	0	0	5,311373	5,311373	5,311373	5,311373
THYMO-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	2,17E-18	2,17E-18	0	0	0	2,17E-18	2,17E-18	2,17E-18	2,17E-18
P-ETH-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1,61E-12	1,61E-12	0	0	0	1,61E-12	1,61E-12	1,61E-12	1,61E-12
1:2-D-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	3,00E-23	3,00E-23	0	0	0	3,00E-23	3,00E-23	3,00E-23	3,00E-23
1-PHE-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	8,67E-31	8,67E-31	0	0	0	8,67E-31	8,67E-31	8,67E-31	8,67E-31
O-PHE-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	1,18E-15	1,18E-15	0	0	0	1,18E-15	1,18E-15	1,18E-15	1,18E-15

	526	527	528	530	531	532	533	534	535	536	538	539	540	541	542	544	545	546	547	548	549	550	551
Temperature C	800	297,696		59,02493	400,0434	40	40	40	40	40	40,02884	40,02884	40	40,08861	40,02884	43,33333	43,37827	96,51832	96,51832	320	43,37827	25	65,59054
Pressure bar	0,8936399	1,01325	0,9625875	0,9281137	0,9625875	0,8936399	0,8936399	20	20	20	0,8936399	0,8936399	0,8936399	0,8936399	0,8936399	49,39404	0,8936399	0,8936399	0,8936399	0,8936399	0,8936399	1,01325	1,01325
Vapor Frac	1	1		1	1	0,8791025	1	0,995838	1	1	0	1	0	2,37E-05	1,44E-06	0	0	0	1	1	0	0	1
Total Flow cum/sec	20,24654	9,497372	0	6,029277	11,79129	5,192589	5,192123	0,0924936	0,1229285	0,2173392	6,93E-04	3,72E-05	4,67E-04	2,34E-04	6,94E-04	2,33E-03	1,72E-03	1,69E-03	3,06125	4,972709	1,31E-03	1,29E-03	0,6455524
Enthalpy J/kmol	-90620000	-108030000		-119350000	-108020000	-125480000	-103260000	-214200000	451139	-93440000	-287070000	-378630000	-287080000	-287080000	-287080000	-286700000	-286790000	-280600000	-239790000	-231780000	-286790000	-288360000	-197170000
Mass Flow kg/hr	10204,72	10204,72	0	10204,72	10204,72	10204,72	8614,989	7165,772	678,4311	7844,203	2360,315	0,19791	1589,726	770,7856	2360,513	7933,24	5854,966	5854,966	5854,966	5854,966	4438,589	4438,589	2608,458
CO2	2,83E+03	2829,389	0	5689,267	5689,267	5689,267	5689,216	5689,072	0	5689,072	0	0,1955005	0,0516254	0,1438752	0,1955005	0	0	0	0	0	0	0	1196,931
CH4	58,25479	58,25479	0	58,25479	58,25479	58,25479	58,25478	58,25476	0	58,25476	0	3,05E-05	8,00E-06	2,25E-05	3,05E-05	0	0	0	0	0	0	0	162,1494
H2O	3568,053	3568,053	0	2397,371	2397,371	2397,371	807,6967	37,05678	0	37,05678	2360,315	0	1589,674	770,6399	2360,315	7933,24	5854,966	5854,966	5854,966	5854,966	4438,589	4438,589	97,01026
N2	4,99E+01	4,99E+01	0,00E+00	49,94813	4,99E+01	4,99E+01	4,99E+01	4,99E+01	0,00E+00	4,99E+01	0,00E+00	3,11E-06	8,12E-07	2,30E-06	3,11E-06	0,00E+00	0,00E+00	0,00E+00	0,00E+00	0,00E+00	0,00E+00	0,00E+00	6,79E-05
CO	2976,647	2976,647	0	1156,454	1156,454	1156,454	1156,454	1156,454	0	1156,454	0	6,88E-05	1,80E-05	5,09E-05	6,88E-05	0	0	0	0	0	0	0	1007,388
H2	717,0417	717,0417	0	848,0391	848,0391	848,0391	848,0391	169,6078	678,4311	848,0389	0	2,04E-04	5,28E-05	1,51E-04	2,04E-04	0	0	0	0	0	0	0	0
O2	3,59E-15	3,59E-15	0,00E+00	3,59E-15	3,59E-15	3,59E-15	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C2H6-02	1,29E-06	1,29E-06	0	1,29E-06	1,29E-06	1,29E-06	1,29E-06	1,29E-06	0	1,29E-06	0	0	2,22E-13	0	2,22E-13	0	0	0	0	0	0	0	35,34009
C2H4-02	3,31E-06	3,31E-06	0	3,31E-06	3,31E-06	3,31E-06	3,31E-06	3,31E-06	0	3,31E-06	0	0	7,81E-13	0	7,81E-13	0	0	0	0	0	0	0	109,6398
SO2	2,92E-06	2,92E-06	0	2,92E-06	2,92E-06	2,92E-06	2,92E-06	2,92E-06	0	2,92E-06	0	2,03E-09	5,42E-10	1,48E-09	2,03E-09	0	0	0	0	0	0	0	0
N-HEX-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N-DOD-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
4-MET-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ETHYL-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-MET-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CYCLO-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N-PRO-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1:3-D-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
4-MET-02	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
INDAN-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-N-H-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
PROPA-01	1,38E-12	1,38E-12	0	1,38E-12	1,38E-12	1,38E-12	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N-BUT-01	1,33E-18	1,33E-18	0	1,33E-18	1,33E-18	1,33E-18	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
N-PEN-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
HYDRO-03	5,311372	5,311372	0	5,311372	5,311372	5,311372	5,310872	5,309489	0	5,309489	0	1,88E-03	4,99E-04	1,38E-03	1,88E-03	0	0	0	0	0	0	0	0
THYMO-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
P-ETH-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1:2-D-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1-PHE-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
O-PHE-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

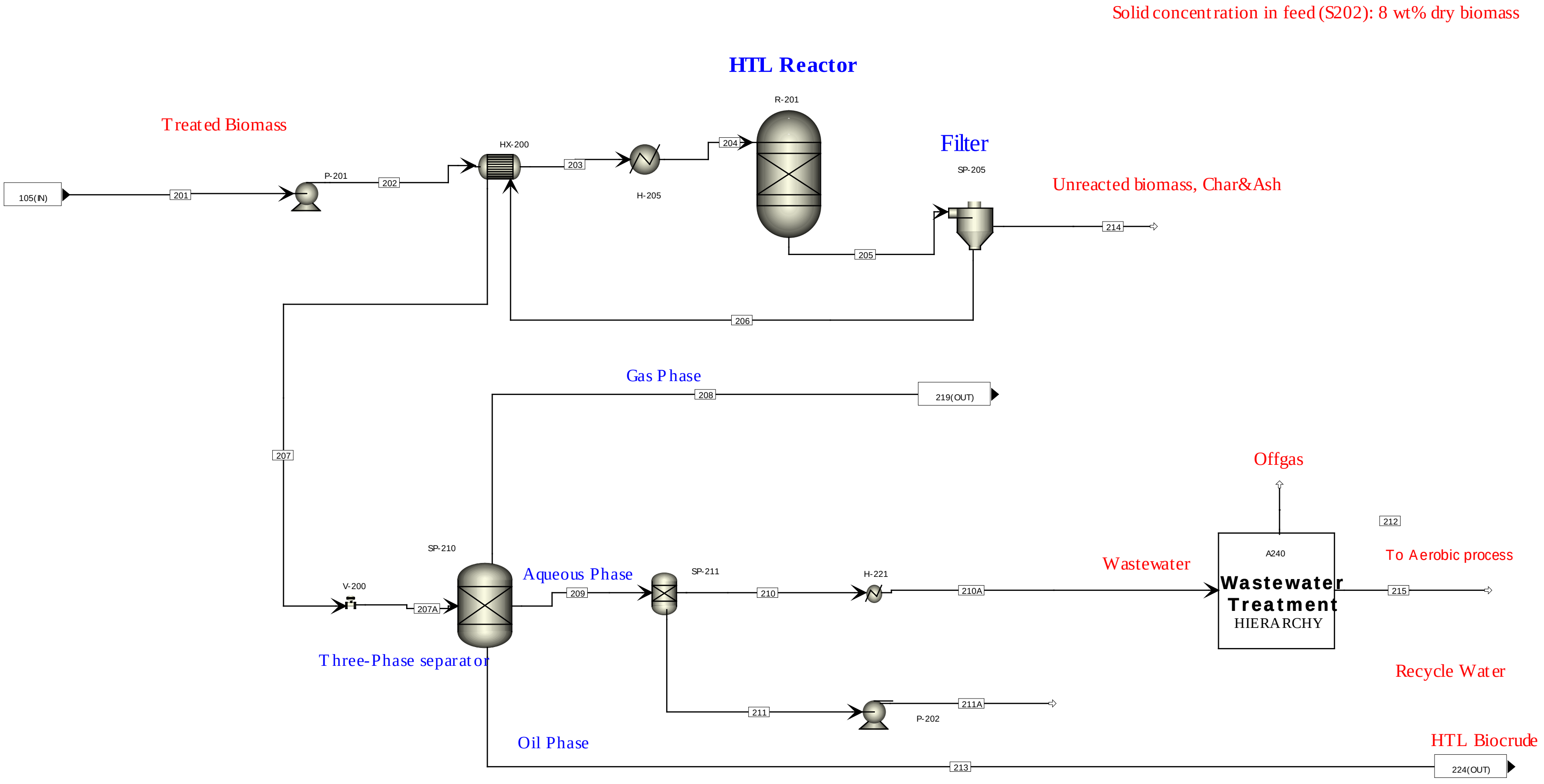
Note: Stream tables are for one train of 500 tDM/day

8.5 Area 100 HTL Feed Handling and Prep



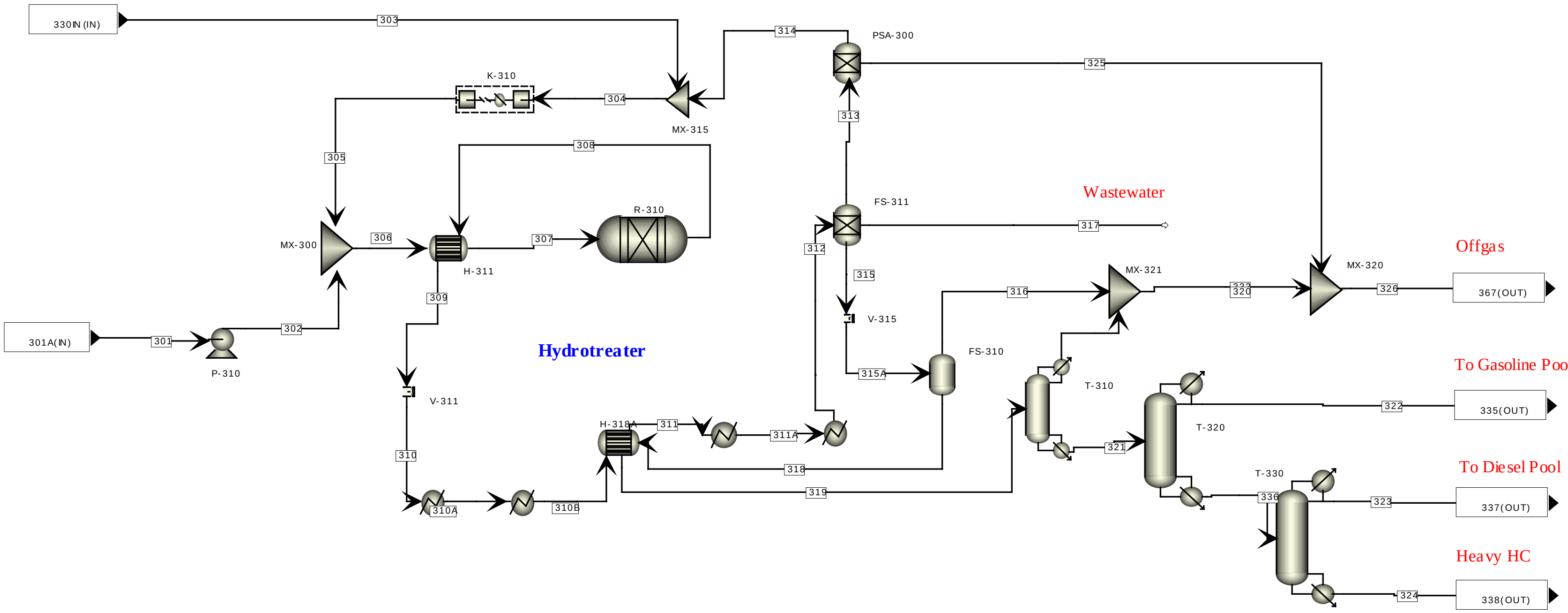
	100	101	225	102	103
Stream	FEED	Pressureized Feed	Water Recycel	8% Solids Mixture	Presurized Mixture
Temperature C	15.6	15.6	117.9	106.3	106.4
Pressure bar	1.013	4.461	4.461	4.461	5.84
Mass Flow kg/hr	41666.0	41666.0	20833.0	41666.0	41666.0
Enthalpy Gcal/hr	-80.054	-80.051	-788.755	-869.481	-869.46
Mass Flow kg/hr					
H2O	20833	20832.999	211780.1	232613.1	232613.069
Temperature C	15.6	15.6		106.3	106.4
Pressure bar	1.013	4.461		4.461	5.84
Vapor Frac	0	0		0	0
Mass Flow kg/hr					
CHAR					
ASH					
WOOD	20833	20833		20833	20833
Mass Frac					
CHAR					
ASH					
WOOD	1	1		1	1

8.6 Area 200 HTL Conversion



Stream No	**201**	**202**	**203**	**204**	**205**	**206**	**207**	**207A**	**208**	**209**	**210**	**210A**	**211**	**212**	**213**	**214**
Stream ID	FEED Slurry	Pressurized Feed Slurry	Preheated Feed Slurry	Reactor Inlet	Reactor Effluent	Solids Filter: Liquid Effluent	Cooled Reactor Effluent	Depressurized Reactor Effluent	Gas Phase	Aqueous Phase to WWT	WW to AD	Cooled Wastewater	To Recycle Water	Offgass	HTL Oil Effluent	Solids Filter: Solids Stream
Temperature, C	106	109	304	355	350	350	144.2	117.8	117.8	117.8	117.8	60	117.8	120.4	117.8	350
Pressure, bar	6	207	206	206	205.81	205.809	205.74	2.068	2.1	2.068	2.068	1.931	2.068	2.068	2.068	205.81
Vapor Frac	0	0	0	0	0.05	0	0	0.417	1	0.033	0.96	0.016	0	1	0.05	0
Enthalpy Gcal/hr	-869.5	-867.7	-809.1	-794.2	-813.0	-813.1	-873.5	-873.5	-7.2	-871.2	-1932.4	-87.7	-788.8	-11.5	-4.1	
Mass Flow kg/hr	**253446.1**	**253446.1**	**253446.1**	**253446.1**	**253446.1**	**251389.7**	**251389.7**	**251389.7**	**3662.3**	**241010.1**	**29209.9**	**29209.9**	**211800.274**	**9081.426**	**7620.971**	**1195.4005**
H2					32.791	32.791	32.791	32.791	32.791					25.421		
CO2					3302.447	3302.447	3302.447	3302.447	3302.447					2751.765		
H2O	232613.1	232613.069	232613.069	232613.07	233145.4	233167.255	233167.255	233167.255		233630.4595	21830.1855	21830.1855	211800.274	120.394	419.701	
H2S														4.01		
NH3														23.68		
CH4					109.08	109.08	109.08	109.08	109.08					1413.964		
C2H6					30.666	30.666	30.666	30.666	93.165							
C3H8					90.265	90.265	90.265	90.265	69.432							
N-C4H10					76.207	76.207	76.207	76.207	55.374							
2-PYRROL					175.789	175.789	175.789	175.789		166.999	166.999	166.999		0.005	8.789	
ETHYLTHI					17.666	17.666	17.666	17.666		16.783	16.783	16.783		0.48	0.883	
METHANOL					544.2	544.2	544.2	544.2		538.758	538.758	538.758		52.857	5.442	
ACEACID					413.535	413.535	413.535	413.535		409.4	409.4	409.4		55.909	4.135	
PROACID					413.535	413.535	413.535	413.535		409.4	409.4	409.4		40.344	4.135	
BUTACTO					205.205	205.205	205.205	205.205		184.685	184.685	184.685		5.144	20.521	
2-BUTANO					410.41	410.41	410.41	410.41		287.287	287.287	287.287		54.641	123.123	
12BENOL					413.535	413.535	413.535	413.535		413.535	413.535	413.535		< 0.001		
13BEN4P					1469.768	1469.768	1469.768	1469.768		881.861	881.861	881.861		0.17	587.907	
23HFDH5M					205.205	205.205	205.205	205.205		203.153	203.153	203.153		4.729	2.052	
26DMPHE					205.205	205.205	205.205	205.205							205.205	
13BEN45M					1026.025	1026.025	1026.025	1026.025		410.41	410.41	410.41		trace	615.615	
PHE-2M4P					2055.175	2055.175	2055.175	2055.175		205.518	205.518	205.518		0.958	1849.658	
CYCLOPEN					410.41	410.41	410.41	410.41							410.41	
CYCPO-2M					410.41	410.41	410.41	410.41		164.164	164.164	164.164		115.307	246.246	
2CYC-2M					307.808	307.808	307.808	307.808		277.027	277.027	277.027		169.286	30.781	
PHENOL					413.535	413.535	413.535	413.535		289.475	289.475	289.475		10.356	124.061	
2CYC23M					205.205	205.205	205.205	205.205		10.26	10.26	10.26		2.958	194.945	
PHENO4M					430.931	430.931	430.931	430.931		258.558	258.558	258.558		11.082	172.372	
C13H12					615.615	615.615	615.615	615.615		61.562	61.562	61.562		1.186	554.054	
C14H14O					820.82	820.82	820.82	820.82		82.082	82.082	82.082		0.406	738.738	
C15H12					1109.128	1109.128	1109.128	1109.128							1109.128	
PYROLIG					82.082	82.082	82.082	82.082							82.082	
FORMIC ACID					2219.756	2219.756	2219.756	2219.756		2108.768	2108.768	2108.768		1765.124	110.988	
CHAR					1765.811											882.9055
ASH					312.495											312.495
WOOD	20833	20833	20833	20833												

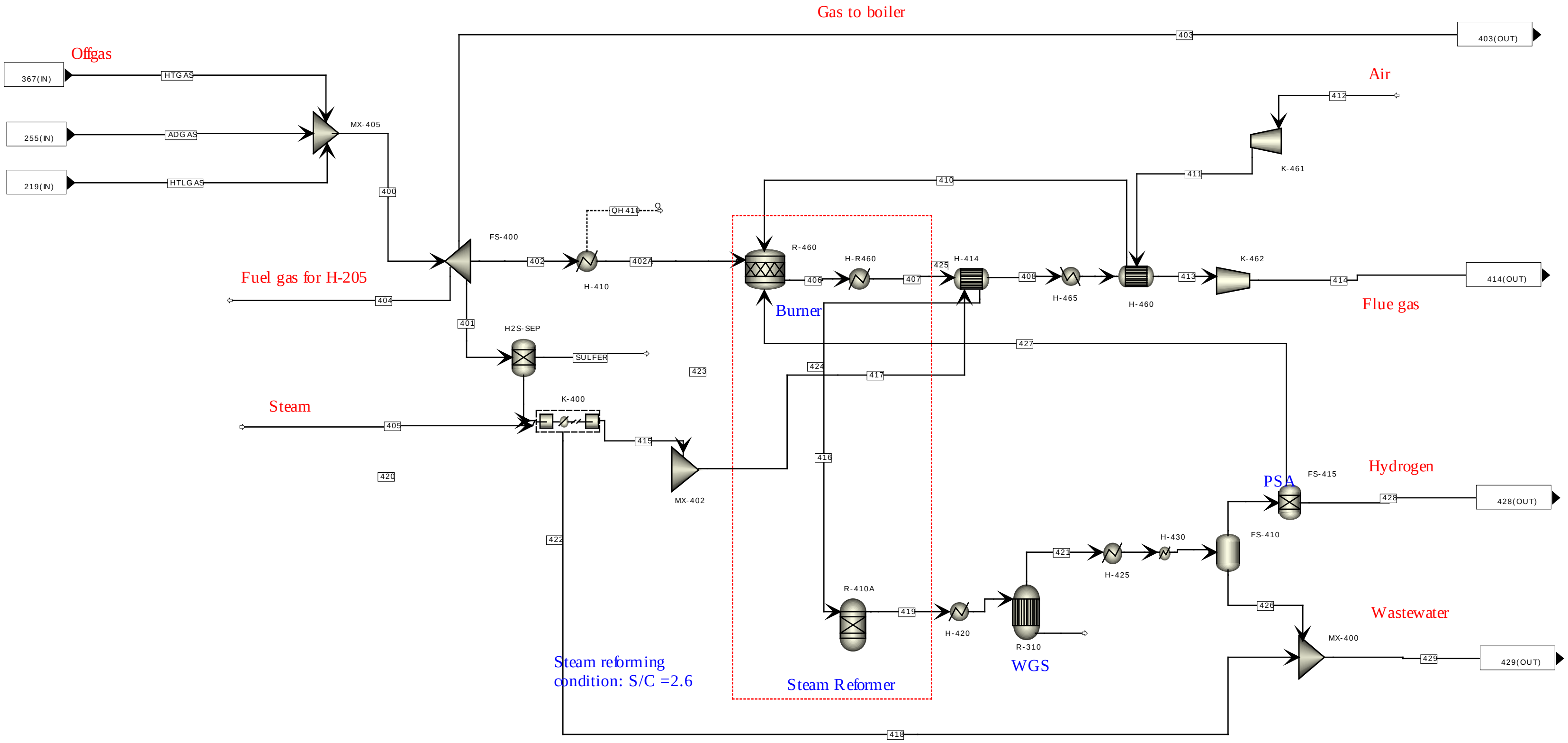
8.7 Area 300 Hydrothermal Liquefaction Biocrude Hydrotreating



Stream No.	**301**	**302**	**303**	**304**	**305**	**306**	**307**	**308**
Stream ID	HTL Bio-oil Feed	Cooled/ Con. B io-oil	Pressurized Feed	Compressed H2	Recycled + Feed H2	Pressurized H2	Bio-oil + H2 Reactor Feed	Heated HTL Oil
Temperature, C	117.8	114.5	116.5	60	53.1	130.6	116.5	165.6
Pressure, bar	2.068	2.068	137.413	29.2	21.698	137.413	137.413	137.068
Vapor Frac	0.05	0	0.735	1	1	1	0.735	0.75
Enthalpy MMBtu/hr	-4.06	-4.098	-3.903	0.029	0.04	0.156	-3.903	-3.607
Mass Flow kg/hr	**7621.0**	**7621.0**	**7621.0**	**237.7**	**411.5**	**411.5**	**8032.5**	**8032.5**
H2				237.736	411.53	411.53	411.532	411.532
H2O	419.701	419.701	419.701				419.701	419.701
H2S								
SO2								
NH3								
NO2								
CH4								
C2H6								
C3H8								
N-C4H10								
N-PENTAN								
HEXANE								
2-PYRROL	8.789	8.789	8.789				8.789	8.789
ETHYLTHI	0.883	0.883	0.883				0.883	0.883
METHANOL	5.442	5.442	5.442				5.442	5.442
ACEACID	4.135	4.135	4.135				4.135	4.135
PROACID	4.135	4.135	4.135				4.135	4.135
BUTACTO	20.521	20.521	20.521				20.521	20.521
2-BUTANO	123.123	123.123	123.123				123.123	123.123
13BEN4P	587.907	587.907	587.907				587.907	587.907
23HFDH5M	2.052	2.052	2.052				2.052	2.052
26DMPHE	205.205	205.205	205.205				205.205	205.205
13BEN45M	615.615	615.615	615.615				615.615	615.615
PHE-2M4P	1849.658	1849.658	1849.658				1849.658	1849.658
CYCLOPEN	410.41	410.41	410.41				410.41	410.41
CYCPO-2M	246.246	246.246	246.246				246.246	246.246
2CYC-2M	30.781	30.781	30.781				30.781	30.781
PHENOL	124.061	124.061	124.061				124.061	124.061
2CYC23M	194.945	194.945	194.945				194.945	194.945
PHENO4M	172.372	172.372	172.372				172.372	172.372
C13H12	554.054	554.054	554.054				554.054	554.054
C14H14O	738.738	738.738	738.738				738.738	738.738
C15H12	1109.128	1109.128	1109.128				1109.128	1109.128
PYROLIG	82.082	82.082	82.082				82.082	82.082
FORMI-01	110.988	110.988	110.988				110.988	110.988
4-MET-01								
N-DOD-01								
ETHYL-01								
1-MET-01								
CYCLO-01								
N-PRO-01								
13-D-01								
4-MET-02								
INDAN-01								
1-N-H-01								
THYMO-01								
P-ETH-01								
12-D-01								
1-PHE-01								

Stream No.	**309**	**310**	**311**	**312**	**312A**	**314**	**315**	**317**	**318**	**319**	**320**	**321**	**322**	**323**	**325**	**326**	**324**
Stream ID	Reactor Effluent	Cooled HT Oil	Depressurized S310	Further Cooling/ Depressurization	Feed to Separators	Recycled H2	Low P Separation Feed	WW Effluent	Product Oil to Distillation	To First Distillation	Offgass	PSA Offgass	Offgass	Gasoline Distillate	Diesel Distillate	Heavy Products	To Second Distillation
Temperature, C	425.7	396.2	365.8	118.5	43.3	43.3	46.4	43.3	46.4	93.3	66.1	43.3	43.8	149.5	317.6	352.8	337.5
Pressure, bar	136.378	136.34	49.987	49.877	49.394	21.7	3.792	49.394	3.792	3.723	3.309	3.426	3.31	1.358	1.082	1.082	1.358
Vapor Frac	1	0.947	0.971	0.524	0.472	1	0	0	0	0	1	1	1	0	0	0	0
Enthalpy MMBt	-3.633	-12.879	-3.93	-5.908	-6.384	0.011	-0.27	-6.1	-0.27	-0.167	-0.01	-0.317	-0.327	-0.542	0.56	0.258	0.836
Mass Flow k	**8032.5**	**8032.5**	**8032.5**	**8032.5**	**8032.5**	**173.8**	**5715.7**	**1601.3**	**5715.7**	**5715.7**	**21.0**	**541.7**	**562.8**	**2601.99**	**2239.15**	**853.52**	**3092.66**
H2	217.245	217.245	217.245	217.245	217.245	173.796						43.449	43.449				
H2O	1601.269	1601.269	1601.269	1601.269	1601.269			1601.269									
H2S	0.284	0.284	0.284	0.284	0.284							0.284	0.284				
SO2																	
NH3	1.762	1.762	1.762	1.762	1.762							1.762	1.762				
NO2																	
CH4	101.439	101.439	101.439	101.439	101.439							101.439	101.439				
C2H6	84.241	84.241	84.241	84.241	84.241							84.241	84.241				
C3H8	73.76	73.76	73.76	73.76	73.76							73.76	73.76				
N-C4H10	29.168	29.168	29.168	29.168	29.168		19.191		19.191	19.191	17.272	9.977	27.249	1.919			
N-PENTAN	8.298	8.298	8.298	8.298	8.298							8.298	8.298				
HEXANE	218.531	218.531	218.531	218.531	218.531							218.531	218.531				
2-PYRROL																	
ETHYLTHI																	
METHANOL																	
ACEACID																	
PROACID																	
BUTACTO																	
2-BUTANO																	
13BEN4P																	
23HFDH5M																	
26DMPHE																	
13BEN45M																	
PHE-2M4P																	
CYCLOPEN																	
CYCPO-2M																	
2CYC-2M																	
PHENOL																	
2CYC23M																	
PHENO4M																	
C13H12																	
C14H14O																	
C15H12																	
PYROLIG																	
FORMI-01																	
4-MET-01	243.574	243.574	243.574	243.574	243.574		243.574		243.574	243.574				243.574	trace	trace	trace
N-DOD-01	262.555	262.555	262.555	262.555	262.555		262.555		262.555	262.555				262.554	0.001	trace	0.001
ETHYL-01	173.033	173.033	173.033	173.033	173.033		173.033		173.033	173.033	0.03		0.03	173.003			trace
1-MET-01	221.022	221.022	221.022	221.022	221.022		221.022		221.022	221.022	0.001		0.001	221.021			trace
CYCLO-01	190.336	190.336	190.336	190.336	190.336		190.336		190.336	190.336	3.738		3.738	186.598			trace
N-PRO-01	190.294	190.294	190.294	190.294	190.294		190.294		190.294	190.294				190.294	trace	trace	trace
13-D-01	277.572	277.572	277.572	277.572	277.572		277.572		277.572	277.572				277.377	0.195	trace	0.195
4-MET-02	1441.738	1441.738	1441.738	1441.738	1441.738		1441.738		1441.738	1441.738				trace	773.081	668.656	1441.738
INDAN-01	493.374	493.374	493.374	493.374	493.374		493.374		493.374	493.374				493.374	< 0.001	trace	< 0.001
1-N-H-01	200.019	200.019	200.019	200.019	200.019		200.019		200.019	200.019				trace	197.816	2.204	200.019
THYMO-01	173.857	173.857	173.857	173.857	173.857		173.857		173.857	173.857				137.442	36.413	0.002	36.415
P-ETH-01	414.838	414.838	414.838	414.838	414.838		414.838		414.838	414.838				414.835	0.003	trace	0.003
12-D-01	400.947	400.947	400.947	400.947	400.947		400.947		400.947	400.947				0.003	399.089	1.856	400.944
1-PHE-01	1013.349	1013.349	1013.349	1013.349	1013.349		1013.349		1013.349	1013.349				trace	832.547	180.802	1013.349

8.8 HTL Hydrogen Plant



Stream ID	HTL Gas	AD Gas	HT Gas	400	401	402	402A	403	404	405	406	407	408	409	410	411	412	413	414	415	416	417	418	419	420	421	422A	423	424	425	426	427	428	429	SULFER
Temperature C	117.8	120.4	43.8	111.5	111.5	111.5	260	111.5	111.5	371.1	1565	899	686.4	232.2	204.4	55.4	32.2	136.9	146.2	136.4	565.6	247.3	57.1	850	315.6	416.6		132.2	60	60	60	60	60	12.4	2.068
Pressure bar	2.068	2.068	3.309	2.068	2.068	2.068	2.062	2.068	2.068	45.45	1.082	1.082	1.075	1.041	1.082	1.22	1.013	1.034	1.103	31.026	30.992	31.026	2.068	30.992	30.957	30.268	30.268	30.234	30.096	30.096	30.096	2.413	30.096	2.068	1
Vapor Frac	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	**1**	1	1	1	1	0.022	1	1	1		0.848	0.766	1	0	1	1	0.009	0.047
Mass Flow kg/hr	3662.289	6630	563	10855.246	3906.106	132.787	132.787	5727.732	1088.621	2462.403	12992.1	12992.1	12992.1	12992.1	8900.186	8900.186	8900.186	12992.1	12992.1	3118.797	5581.2	5581.2	785.59	5581.2	5581.2	5581.2	0	5581.2	5581.2	4196.863	1384.337	3959.127	237.736	2169.927	0.719
Enthalpy Gcal/hr	-7.22	-11.5	-0.3	-19.1	-6.9	-0.2	-0.2	-10.075	-1.915	-7.552	-7.932	-10.797	-11.662	-13.364	-0.173	-0.501	-0.551	-13.692	-13.661	-5.546	-12.234	-13.1	-1.458	-9.368	-10.958	-10.958		-12.231	-12.742	-7.516	-5.226	-7.532	0.028	-6.71	
Mass Flow kg/hr																																			
H2	32.791	25.421	43.449	101.661	36.581	1.244	1.244	53.641	10.195											36.57	36.57	36.6	0.011	233.024	233.024	297.173		297.173	297.173	297.17	0.002	59.434	237.736	0.013	
CO																								1377.921	1377.921	486.584		486.584	486.584	486.583	0.001	486.583		0.001	
N2											6597.403	6597.403	6597.403	6597.403	6590.427	6590.427	6590.427	6597.403	6597.403					6.977	6.977	6.977		6.977	6.977	6.977	< 0.001	6.977		< 0.001	
O2											337.712	337.712	337.712	337.712	2019.319	2019.319	2019.319	337.712	337.712																
AR											112.406	112.406	112.406	112.406	112.406	112.406	112.406	112.406	112.406																
CO2	3302.447	2751.765		6054.212	2178.522	74.058	74.058	3194.484	607.148		4676.932	4676.932	4676.932	4676.932	4.379	4.379	4.379	4676.932	4676.932	2160.386	2160.386	2160.386	18.136	1775.004	1775.004	3175.469		3175.469	3175.469	3174.905	0.564	3174.905		18.699	
H2O		120.394		120.394	43.322	1.473	1.473	63.525	12.074	2462.403	1267.144	1267.144	1267.144	1267.144	173.656	173.656	173.656	1267.144	1267.144	23.73	2486.132	2486.132	19.592	1989.14	1989.14	1415.864		1415.864	1415.864	32.284	1383.58	32.284		1403.173	1.545
H2S		4.01	0.284	4.294	1.545	0.053	0.053	2.266	0.431																										
SO2											0.102	0.102	0.102	0.102				0.102	0.102																
NH3		23.68	1.762	25.442	9.155	0.311	0.311	13.424	2.551		0.401	0.401	0.401	0.401				0.401	0.401	8.758	8.758	8.758	0.397	0.275	0.275	0.275		0.275	0.275	0.09	0.185	0.09		0.582	
NO2																																			
CH4	109.08	1413.964	101.439	1624.482	584.547	19.872	19.872	857.152	162.912											583.664	583.664	583.664	0.882	198.837	198.837	198.837		198.837	198.837	198.834	0.004	198.834		0.886	
C2H6	93.165		84.241	177.406	63.837	2.17	2.17	93.608	17.791											63.298	63.298	63.298	0.54	0.02	0.02	0.02		0.02	0.02	0.02	trace	0.02		0.54	
C3H8	69.432		73.76	143.192	51.526	1.752	1.752	75.555	14.36											50.334	50.334	50.334	1.191											1.191	
N-C4H10	55.374		27.249	82.623	29.731	1.011	1.011	43.596	8.286											27.947	27.947	27.947	1.784											1.784	
N-PENTAN			8.298	8.298	2.986	0.102	0.102	4.378	0.832											2.579	2.579	2.579	0.407											0.407	
HEXANE			218.531	218.531	78.635	2.673	2.673	115.307	21.915											58.509	58.509	58.509	20.127											20.127	
CARBON																																			
SULFUR																																			
2-PYRROL		0.005		0.005	0.002	< 0.001	< 0.001	0.003	0.001		< 0.001	< 0.001	< 0.001	< 0.001				< 0.001	< 0.001				0.002											0.002	0.173
ETHYLTHI		0.48		0.48	0.173	0.006	0.006	0.253	0.048																										
METHANOL		52.857		52.857	19.02	0.647	0.647	27.89	5.301											8.577	8.577	8.577	10.443											10.443	
GLYACID																																			
ACEACID		55.909		55.909	20.118	0.684	0.684	29.5	5.607											0.465	0.465	0.465	19.653											19.653	
PROACID		40.344		40.344	14.517	0.494	0.494	21.287	4.046											0.036	0.036	0.036	14.481											14.481	
BUTACTO		5.144		5.144	1.851	0.063	0.063	2.714	0.516											< 0.001	< 0.001	< 0.001	1.851											1.851	
2-BUTANO		54.641		54.641	19.662	0.668	0.668	28.831	5.48											7.235	7.235	7.235	12.427											12.427	
12BENOL		< 0.001		< 0.001	< 0.001	trace	trace	< 0.001	trace														< 0.001											< 0.001	
13BEN4P		0.17		0.17	0.061	0.002	0.002	0.09	0.017														0.061											0.061	
23HFDH5M		4.729		4.729	1.702	0.058	0.058	2.495	0.474											trace	trace	trace	1.702											1.702	
26DMPHE																																			
13BEN45M		trace		trace	trace	trace	trace	trace	trace														trace											trace	
PHE-2M4P		0.958		0.958	0.345	0.012	0.012	0.505	0.096											trace	trace	trace	0.345											0.345	
CYCLOPEN																																			
CYCPO-2M		115.307		115.307	41.492	1.411	1.411	60.842	11.564											0.737	0.737	0.737	40.755											40.755	
2CYC-2M		169.286		169.286	60.915	2.071	2.071	89.323	16.977											0.32	0.32	0.32	60.596											60.596	
PHENOL		10.356		10.356	3.726	0.127	0.127	5.464	1.039											< 0.001	< 0.001	< 0.001	3.726											3.726	
2CYC23M		2.958		2.958	1.064	0.036	0.036	1.561	0.297											< 0.001	< 0.001	< 0.001	1.064											1.064	
PHENO4M		11.082		11.082	3.988	0.136	0.136	5.848	1.111											trace	trace	trace	3.988											3.988	
C13H12		1.186		1.186	0.427	0.015	0.015	0.626	0.119											trace	trace	trace	0.427											0.427	
C14H14O		0.406		0.406	0.146	0.005	0.005	0.214	0.041														0.146											0.146	
C15H12																																			
FORMI-01		1765.124		1765.124	635.155	21.592	21.592	931.361	177.016											85.083	85.083	85.083	550.072											550.072	
4-MET-01			trace	trace	trace	trace	trace	trace	trace											trace	trace	trace	trace											trace	
N-DOD-01			trace	trace	trace	trace	trace	trace	trace																										
ETHYL-01			0.03	0.03	0.011	< 0.001	< 0.001	0.016	0.003											0.003	0.003	0.003	0.008											0.008	
1-MET-01			0.001	0.001	< 0.001	< 0.001	< 0.001	0.001	< 0.001											< 0.001	< 0.001	< 0.001	< 0.001											< 0.001	
CYCLO-01			3.738	3.738	1.345	0.046	0.046	1.972	0.375											0.568	0.568	0.568	0.777											0.777	
N-PRO-01			trace	trace	trace	trace	trace	trace	trace											trace	trace	trace	trace											trace	
13-D-01			trace	trace	trace	trace	trace	trace	trace																										
4-MET-02			trace	trace	trace	trace	trace	trace	trace																										
INDAN-01			trace	trace	trace	trace	trace	trace	trace														trace											trace	
1-N-H-01			trace	trace	trace	trace	trace	trace	trace																										

Pacific Northwest
NATIONAL LABORATORY

U.S. DEPARTMENT OF
ENERGY

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99352
1-888-375-PNNL (7665)
www.pnl.gov