PNNL-23591

U.S. DEPARTMENT OF ENERGY

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Low-Severity Hydroprocessing to Stabilize Bio-oil: TechnoEconomic Assessment

IJ Tews
DC Elliott

August 2014

Pacific Northwest
NATIONAL LABORATORY

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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

Bio-oil – liquid product of fast pyrolysis

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

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

1.0 Introduction

The impetus for this study was the suggestion that recent developments in fast pyrolysis (FP) bio-oil production had indicated instability of the bio-oil in storage which might lead to unacceptable viscosity increases. Commercial operation of FP in Finland began in 2014 and the distribution of the bio-oil to isolated users has been proposed as the long-term plan. Stability of the shipped bio-oil therefore became a concern. Experimental results at PNNL with low-severity hydroprocessing of bio-oil for stabilization has validated a process in which the stability of the bio-oil could be improved, as measured by viscosity increase following storage of the product at 80 °C for 24h.

In the work reported here the assessed process configuration consists of fast pyrolysis followed by low temperature and pressure hydroprocessing to produce a stable fuel oil product. The product could then be stored for an extended period of time without significant viscosity increase. This work was carried out as part of a collaborative project between Technical Research Centre of Finland (VTT) and Pacific Northwest National Laboratory (PNNL). 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 evaluation of the process developed in earlier collaboration and jointly invented by VTT and PNNL researchers.

Based on previously conducted low-severity hydroprocessing experiments and the recent completion of a comparative TEA,[1] an Aspen Plus® based model for the innovative low-severity hydroprocessing method to stabilize fast pyrolysis bio-oil was developed. Including the FP model from the comparative TEA, this model represents a complete standalone bio-oil production and stabilization plant. The assessed process configuration consists of fast pyrolysis (FP) followed by hydroprocessing to produce a stable fuel oil product, which could be stored on site for extensive periods of time, if necessary. Forest residue wood biomass was the feedstock used in the model.

The modeling effort described is an extension of the previously developed Biomass Direct Liquefaction comparative TEA.[1] Specifically, models developed under that effort included FP and upgrading by multi-stage hydroprocessing and hydrothermal liquefaction and hydrotreating. In both cases the end product was a liquid hydrocarbon and not a stabilized oil, as is the case in this analysis. Modeling techniques, data assessment and economic analysis of all models was completed on the same basis such that all could be compared.

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[1] Tews, I.J.; Onarheim, K., et al. Biomass Direct Liquefaction Options: TechnoEconomic Assessment. PNNL-xxxxx, March 2014, Pacific Northwest National Laboratory, Richland, Washington.

2.0 Analysis Approach

A technoeconomic assessment (TEA) is the standard tool for an investor in evaluating possible processing alternatives. The accuracy of this tool is dependent on the quality and reliability of the data at hand. Technoeconomic viability of process concepts, which haven't been demonstrated, is difficult to evaluate.

Aspen Plus® simulates steady-state chemical process reactions and calculates mass and energy balances based on user input. In this case the data used to establish operating conditions and conversion parameters was experimentally derived. 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 validated by PIs and then used to complete a TEA. Discrepancies in the energy balances are largely due to limitations of Aspen Plus® modeling software and specified physical property sets being used to calculate heats of reaction. The original use for this software is in the petrochemical industry which over many decades has a well-established knowledge of representative modeling components in several databases. The use of the software is this application wherein the heats of reaction for all the thermochemical processing steps of wood residue conversion have not been determined requires assumptions with uncertainties, which lead to error.

In order to model the FP technology, a model compound list needed to be defined to represent the products of the liquefaction step and also the low-severity hydroprocessed (stabilized) product. The organic products are a complex mixture of hundreds of compounds. The number and type of compounds used in the Aspen Plus® model to represent the organic liquid products must reasonably match several key properties such as elemental composition (C, H, O, N, S), quality based on GCMS data, density, and heating value. A significant effort and time was spent on development and refining of these lists in the previous study[1] and these were used here.

The model compound list for FP bio-oil is 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 Plus® since there is no lignin oligomer component in the Aspen data base.

Since the hydroprocessing step was low-severity, the chemical changes in the bio-oil were minimal and the same list of components could be used for the stabilized product.

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 were based on extensive research conducted on biomass material at VTT. Chipped forest residue was assumed as the raw material for the FP process. **Table 2** shows the specification of the feedstock as a summary. Moisture content of the received biomass feedstock is assumed to be at 50%.

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. 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

Size reduction and particle drying for FP is well understood. The plant capacity was set at processing a total of 2000 metric tons per day (474 MW HHV) of bone-dry biomass. This capacity was chosen such that the studies will be on a basis similar to those developed by the Bioenergy Technologies Office of U.S. Department of Energy. In the model, the 2000 metric tons per day are processed through four 500 mtpd reactor units for FP. The reactor size was based on literature reports and previous publications by Jones et al. regarding reactor size for fast pyrolysis.[2] The plant is assumed to be an established "nth" plant design rather than a first of its kind (pioneer) plant.

Upgrading of the FP bio-oil product is still in the early stages of research & development. The 3-stage hydroprocessing model used in the earlier study for fast pyrolysis bio-oil upgrading to liquid hydrocarbon fuels was replaced in this model with a single-stage hydroprocessing at low-severity conditions (lower temperature and pressure with higher space velocity). The exothermic nature was not adequately modeled here, so that the full impact is not incorporated, but the low level of severity implies that the impact of the exothermic reactions will be minimal. A single stage of hydroprocessing for the FP bio-oil for stabilization has been tested in the laboratory, but there is no long-term validation of the method assumed here. The long-term catalyst lifetimes assumed here have not been demonstrated for the bio-oil hydroprocessing.

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[2] 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.

3.0 Process Design for Biomass Conversion to Liquids

The process model developed in this study considered the following processing steps to all be included on-site: raw material preprocessing, pyrolysis, stabilization (low-severity hydroprocessing) and storage. Necessary hydrogen for stabilization is purchased instead of produced on-site due to the small quantities required. Heat input to the fast pyrolysis process is generated in the char combustor. In previous cases, integrated heating was explored for the stabilization/upgrading process steps. However, since the stabilization process used here will occur at lower temperatures heat integration was not considered in this model. **Figure 1** shows the block diagram for the process. Fast pyrolysis reactor yields used to develop these models have been based on previously published experimental results[3] by VTT. Stabilization reactor yields used in model development were based on experimental results, as well.[4]

Biomass Pretreatment

The first step in biomass pretreatment for the FP 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 FP 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.

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 combustor. 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-fired 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 cooled and condensed at 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 flared without heat integration. **Figure 2** shows the FP process that was modeled.

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

[4] Oasmaa, A.; Elliott, D.C. Process for stabilizing fast pyrolysis oil and stabilized fast pyrolysis oil. patent application U.S. 2012/0285079 A1, November 15, 2012.

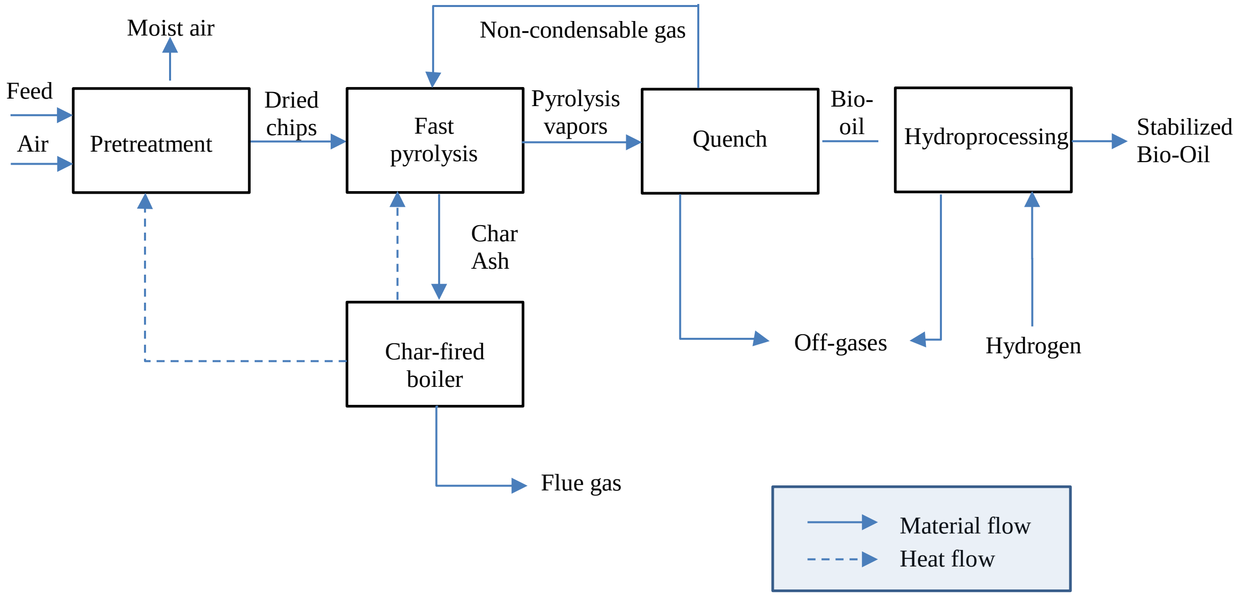

Figure 1. Fast pyrolysis and bio-oil stabilization process flow diagram

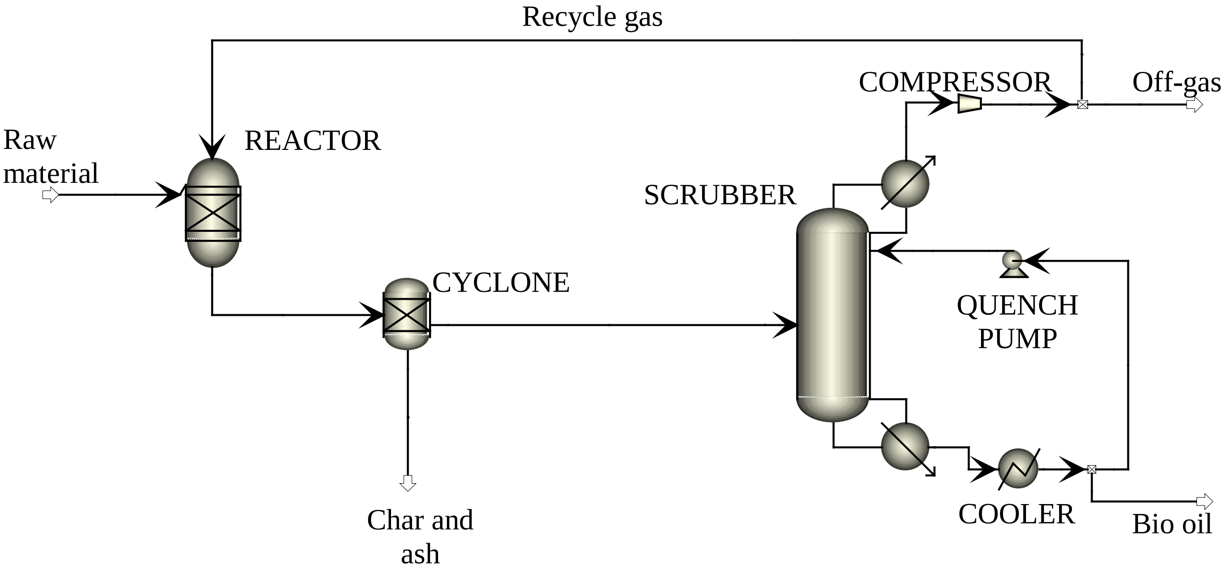

Figure 2 Unit Operations in the Fast Pyrolysis Plant

The fast pyrolysis products are detailed in **Tables 1-3.**

Table 1. Fast Pyrolysis Yield, wt% Based on Dry Biomass Feedstock

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

Table 2. Bio-oil Composition

Bio-oil Components		wt%
Organic phase		71.3
Water		28.7

Table 3. 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 Stabilization

Bio-oil produced in the FP process is unstable and cannot be directly blended with conventional fossil fuels. For this model the bio-oil is put through a stabilization process where hydrogen is used to upgrade the unstable oil by low-severity hydroprocessing.

Liquids produced from biomass by FP are usually upgraded through a catalyzed reaction process where the oxygenated product is exposed to hydrogen under elevated pressure and high temperature.[5] This process reduces the oxygen content via hydrodeoxygenation and decarboxylation reactions such that the resulting concentration is below 1% at severe processing conditions. 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.

Low severity stabilization of the FP bio-oil is similar to the upgrading processes described above. However, for stabilization purposes the bio-oil is pumped to a lower pressure of 10 MPa while being combined with compressed hydrogen. The liquid hourly space of 0.50 volume of oil per volume of catalyst bed per hour is used in this model. Processing at this higher than normal rate for bio-oil HDO

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

occurs at a significantly lower temperature of 85 °C compared to 400 °C used for complete deoxygenation. This low-severity hydroprocessing method has been proven in lab scale experiments at PNNL. It is graphically presented in **Figure 3.** The water content of raw pyrolysis bio-oil from the earlier model and used here was higher (29%) than the bio-oil actually used in the experimental tests for stabilization (22%). Increasing the stabilized product moisture content to 34% is an acceptable assumption as some water formation occurred in the stabilization reaction.[4] Water percentage is the first component of the product stream to be manipulated in order to achieve an elemental balance using Aspen Plus. The Solver Function in EXCEL is used to achieve a finished elemental balance based on the 10+ compounds used to represent the stream.

Since the FP bio-oil effluent temperature is close to the lower operating reaction temperature for hydroprocessing, integrated heating is not addressed in this model as it was in previous work. Minimal temperature increase is needed and accomplished by traditional heat exchangers. The bio-oil is only marginally changed in composition upon stabilization in the HT reactor. Experiments have shown that the bio-oil is sufficiently stable post single stage processing utilizing a Ru on carbon catalyst.

Although this plant does not include reforming of byproduct gases or natural gas but rather uses purchased H_2, off-gas from the hydrotreater is still sent to a Pressure Swing Adsorption (PSA) system and 90% 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 hydroprocessing reactor. The low pressure PSA tail gas stream is waste.

Stabilized bio-oil produced after hydrotreating comes out as a single phase product. **Table 4** below indicates the composition of the product and gas phase on wt% basis and carbon basis. Primary changes to the bio-oil composition occurred in the reduction of sugars such as levoglucosan, as well as some carbonyl compounds.

Table 4. Low Severity Stabilization Yield, wt% and carbon basis

Products		mass	carbon basis
Stabilized Product		96.8	94.9
Gas		3.2	5.1

Table 5. Bio-oil Composition wt.%

Bio-oil Components		wt%
Organic Phase		66
Water		34

Table 6. Gas Composition, mole %

Gas Component		mole %
CO_2		8
CO		8
CH_4		79
Ethylene		3
Ethane		3

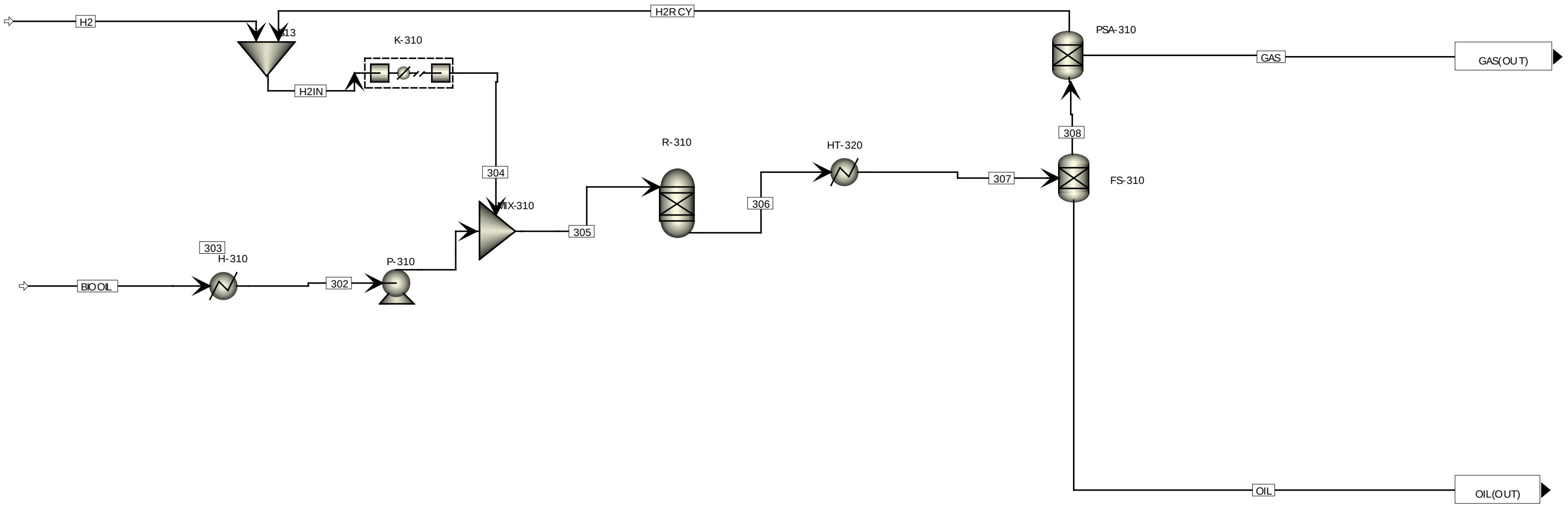

Figure 3. Hydroprocessing for bio-oil stabilization

4.0 Process Mass and Energy Balances

Using Aspen Plus® models, overall mass and energy balance could be generated for the process. The model was based on relevant information including technical information from literature, as well as experimental values.

The mass balance for fast pyrolysis and bio-oil stabilization is depicted in **Figure 4**.

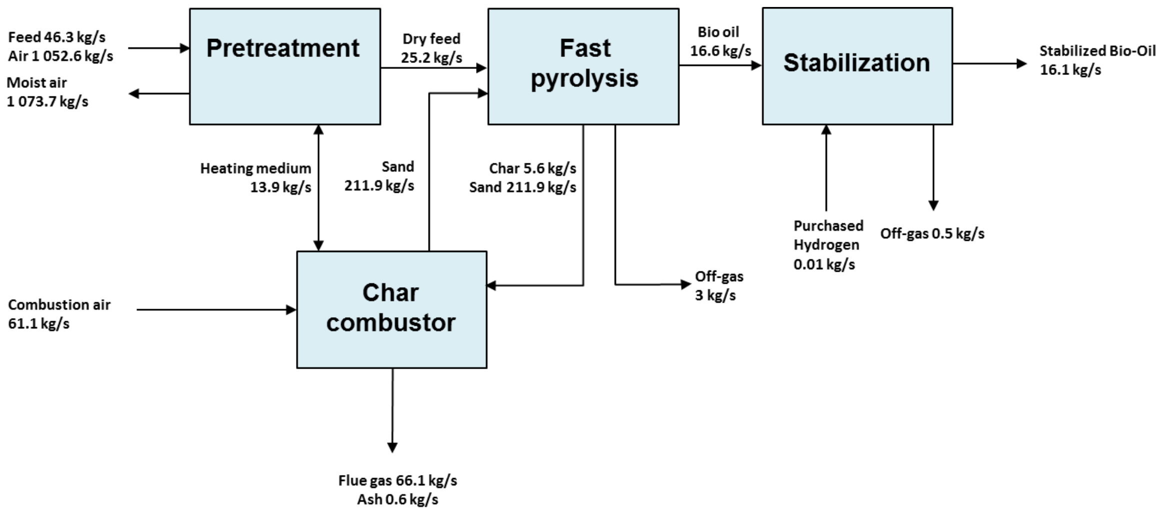

Figure 4. Mass Balance for the Fast Pyrolysis and Stabilization Process

The tabular form of the mass balance data for fast pyrolysis and bio-oil stabilization is given in **Table 4.** The overall mass balance for fast pyrolysis and stabilization shows a 64% yield (16.1/25.2 kg/s) of stabilized bio-oil on the basis of the biomass fed to the FP unit.

Table 4. Mass Balance for the Fast Pyrolysis Pathway

kg/s	**IN**	**OUT**
Wet forest residue	46.3	
Combustion air	61.1	
Purchased H_2	0.01	
Stabilized Bio-Oil		16.1
Flue gas		66.1
Moisture		21.1
Off-gas		3.5
Ash		0.6
TOTAL	**107.4**	**107.4**

The energy balance for fast pyrolysis and bio-oil stabilization is depicted in **Figure 5**.

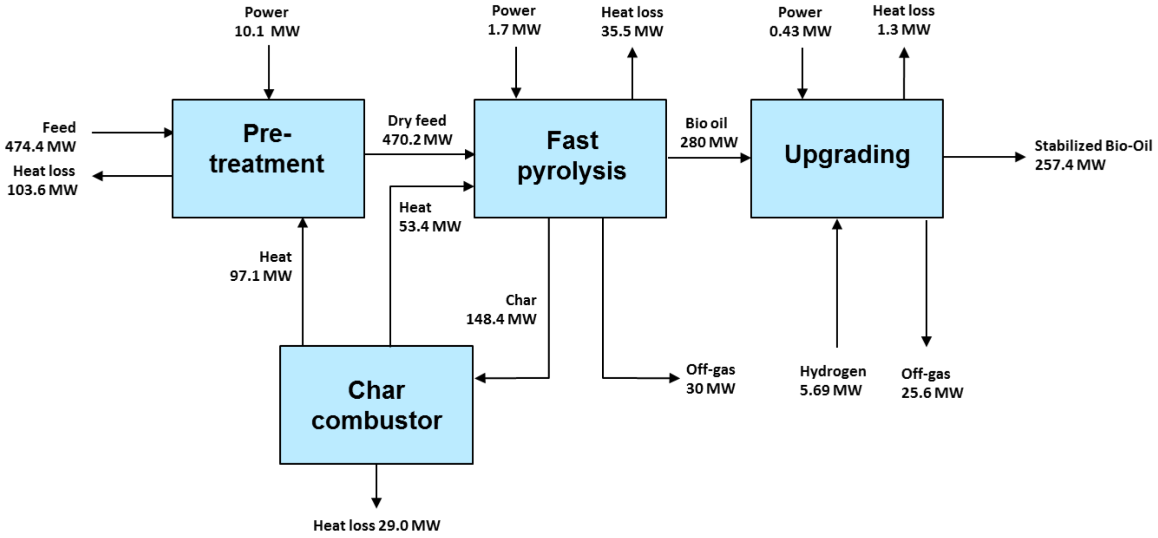

Figure 5. Energy balance (HHV basis) for Fast Pyrolysis and Bio-oil Stabilization

The overall energy balance for the FP process is off by 2%. The energy balance discrepancies for individual blocks range from 0.01 – 5.0%. It is believed that these are largely due to limitations of Aspen Plus® modeling software and specified physical property sets being used to calculate heats of reaction. The original use for this software is in the petrochemical industry with well-defined components. The use of the software in this application, wherein the heat of reaction for pyrolysis and for the hydrotreater as calculated in Aspen Plus® does not quite match experimental results and would need to be further investigated. Furthermore, the choice of compounds used to represent the bio-oil and stabilized bio-oil products and their heats of reaction are limited to classes of compounds and need better definition and detail.

The lower heating values for calculating the overall process efficiency for fast pyrolysis and bio-oil stabilization are given in **Table 5** The overall energy efficiency of fast pyrolysis and bio-oil stabilization shows a 56.4% 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 5. Input and output for Low-Severity Hydrotreating of Fast Pyrolysis Bio-oil based on LHV

	IN	OUT
Feedstock	387.5	
Power	12.2	
Stabilized Bio-Oil		226.4
Off Gas		29.5
Heat loss		143.8
TOTAL	399.7	399.7

5.0 Cost Estimation

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.[2] (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.[2] Installation factors used in the cost analysis of the equipment were obtained by several methods. Primary sources include Harris Group[6], SRI PEP 2007 Yearbook[7] as well as Aspen Capital Cost Estimator.[8] Values were either obtained directly or calculated based on equipment costs provided by the source.

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 fixed installed capital investment (FCI) costs (described above) 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
- hydrogen gas
- electricity consumption
- catalyst costs
- waste handling

Parameters used in the assessment are summarized in **Table 6** below. The higher than normal cost for hydrogen is based on a quote for delivered hydrogen in the small quantities required here.

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[6] 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

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

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

Table 6. 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
Hydrogen cost	7	¢/SCF

The capital costs are grouped into the subsections of the process and presented in **Table 7** below.

Table 7. Fast Pyrolysis and Bio-oil Upgrading Capital Costs (millions of $)

Process Section	PID	Installed	Uninstalled	
Feedstock Handling and Prep	A100	$ 21.4	$ 8.7	8%
Fast Pyrolysis	A100	$ 210	$ 61.9	80%
Hydroprocessing	A310	$ 26.0	$ 10.5	11%
Utilities	A700	$ 1.4	$ 1.0	1%
Total		**$ 259**	**$ 82.1**	**100%**

A summary of the production cost estimate for the FP and stabilization case is shown in **Table 8**. The costs are given for both the primary FP step only, as well as FP combined with the additional fixed and variable costs for stabilization of the bio-oil. Catalyst replacement cost is indicated in the table also. The catalyst lifetime is assumed at one year. The total costs of the finished product, for both primary bio-oil production, as well as stabilized bio-oil production, are calculated in the bottom row.

Table 8. Fast Pyrolysis production cost estimate

	Fast Pyrolysis			Stabilization		
	M $/a	$/t	$/GJ	M $/a	$/t	$/GJ
FIXED OPERATING COST						
Operating labor	1.1	3	0.2	0.3	1	0.1
Maintenance labor	2.3	6	0.4	0.3	1	0.0
Overheads	4.6	11	0.7	0.5	1	0.1
Maintenance materials	7.0	17	1.1	0.8	2	0.1
Taxes, insurance	4.6	11	0.7	0.5	1	0.1
Others	2.3	6	0.4	0.3	1	0.0
Total	22	52	3.5	2.8	7	0.5
MATERIAL COST						
Purchased H_2				4.1	11	0.8
Stabilization catalyst				4.6	10	0.7
Total				8.7	21	1.5
VARIABLE OPERATING COST						
Feedstock	35.0	84	5.6	96.7	238	16.6
Electricity	5.7	14	0.9	0.2	1	0.0
Total	40.7	98	6.5	97.0	239	16.6
CAPITAL CHARGES	34.0	81	5.5	4.0	10	0.7
PRODUCTION COST	**96.7**	**231**	**15.5**	**112.5**	**277**	**19.3**

6.0 Discussion and Conclusions

Comparison of Fast Pyrolysis and Stabilization Costs

The driver behind the development of this cost model was to determine the additional expense of stabilization of fast pyrolysis bio-oil. The comparison of interest is the FP process alone and the FP process followed by the low-severity hydroprocessing to stabilize the bio-oil for long term storage. The comparison of efficiencies and costs are presented in **Table 9**.

Low-severity hydroprocessing of the FP bio-oil results in only a slight loss of energy efficiency compared to the FP process alone, as the majority of the material is recovered in the final liquid product. Low-severity hydroprocessing has a slightly higher investment in capital required with the inclusion of the hydroprocessing plant. The additional operating costs for the stabilization step are minor, but, overall, there is an increased cost for the stabilized bio-oil versus the raw bio-oil.

Table 9. Comparison of the Results for Fast Pyrolysis versus Stabilization

	FP	FP + Stabilization
Energy efficiency to liquid product, LHV	60.2	58.4
Fixed Capital Investment, $M	232	259
Liquid product mass yield, % feed, dry basis	63.5	61.5
Liquid product cost, $/GJ	16.0	19.3
Liquid product cost, $/metric ton	231	277

Uncertainties Needing Further Research

Hydrogen need in this processing plant would be minimal based on experimental data. As a result building a small scale hydrogen production facility would be unrealistic and purchasing the commodity would be preferable. In the previous model (2000 tpd Fast Pyrolysis and Upgrading) hydrogen was produced through reforming of process gases and natural gas. However, because capital investment would not be justified in contrast to the cost of purchased hydrogen, the production plant was not designed in this model. The byproduct gases from pyrolysis and upgrading need to be utilized effectively to improve the process economics and efficiency.

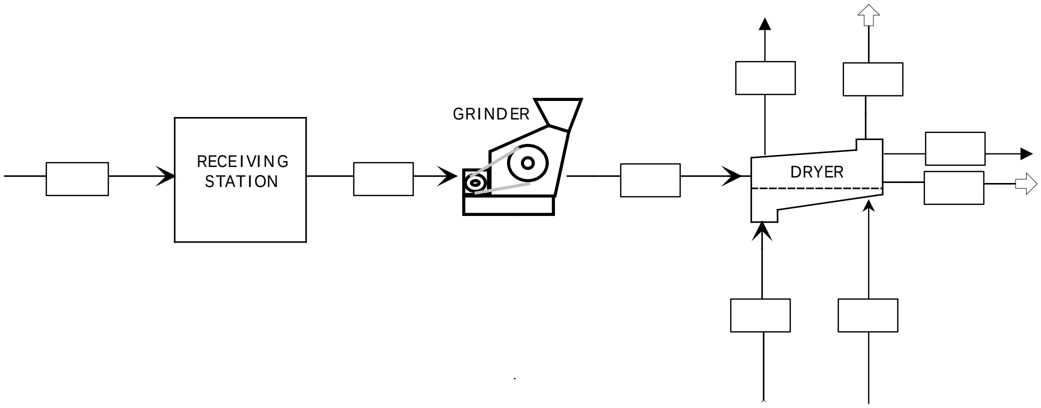
Discrepancies in the energy balances of the model are believed to be largely due to limitations of Aspen Plus® modeling software and specified physical property sets being used to calculate heats of reaction. The use of the software is this application wherein the heats of reaction for all the thermochemical processing steps of wood residue conversion have not been determined requires assumptions with uncertainties, which lead to error. More precise determination of this information will provide the more accurate data to improve the model.

7.0 Appendix

The following sections provide the process diagrams and the data tables from the Aspen Plus® modeling of fast pyrolysis and bio-oil stabilization.

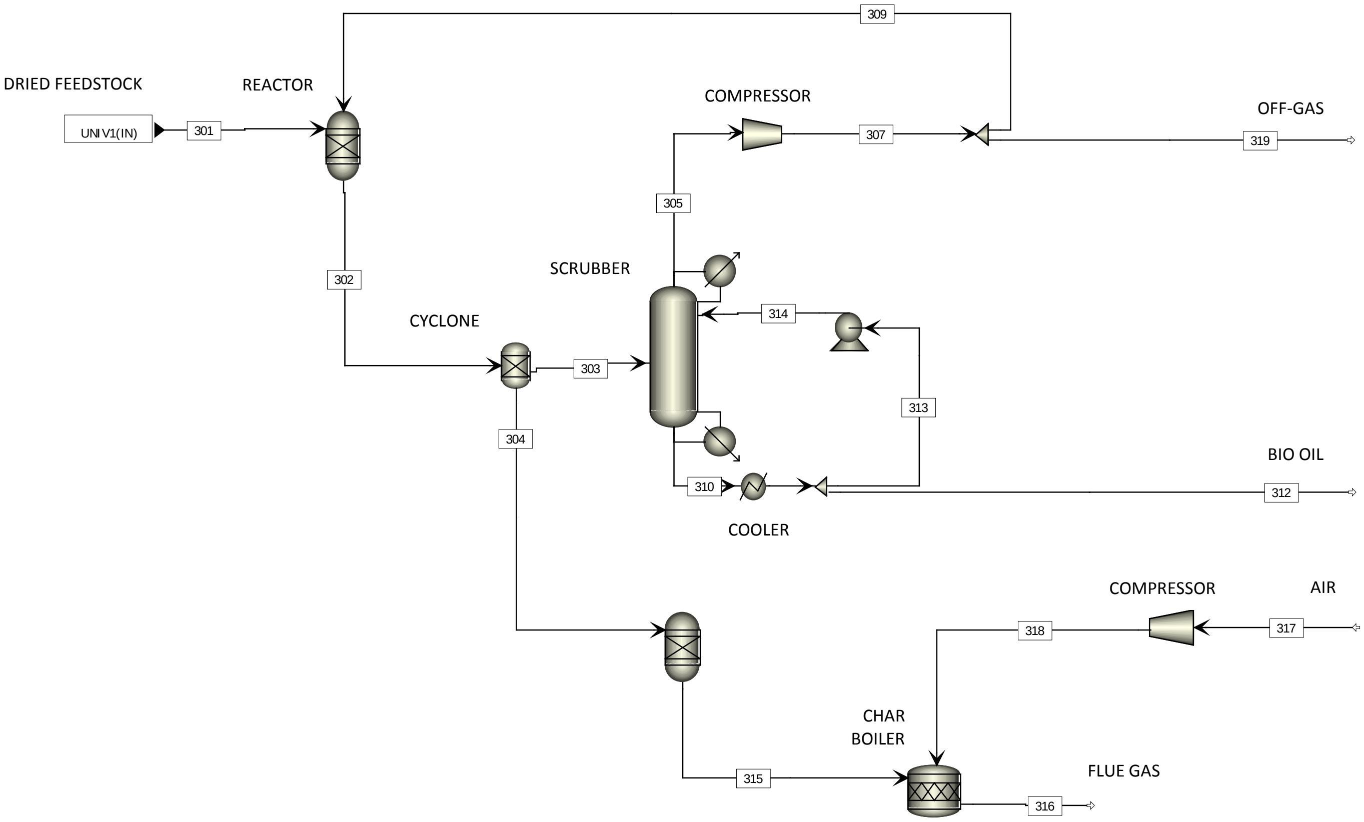
Note: Quantities in stream tables are for one train of 500 tDM/day

7.1 FP pre-treatment



Stream no.	100	101	102	103	104	105	106	107	108
Temperature	25	25	25	25	0	25	25	127,4	120,3
Pressure ba	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: N									
Mass Flow k									
WOOD	20835	20835	20835	20835	0	0	0	0	0

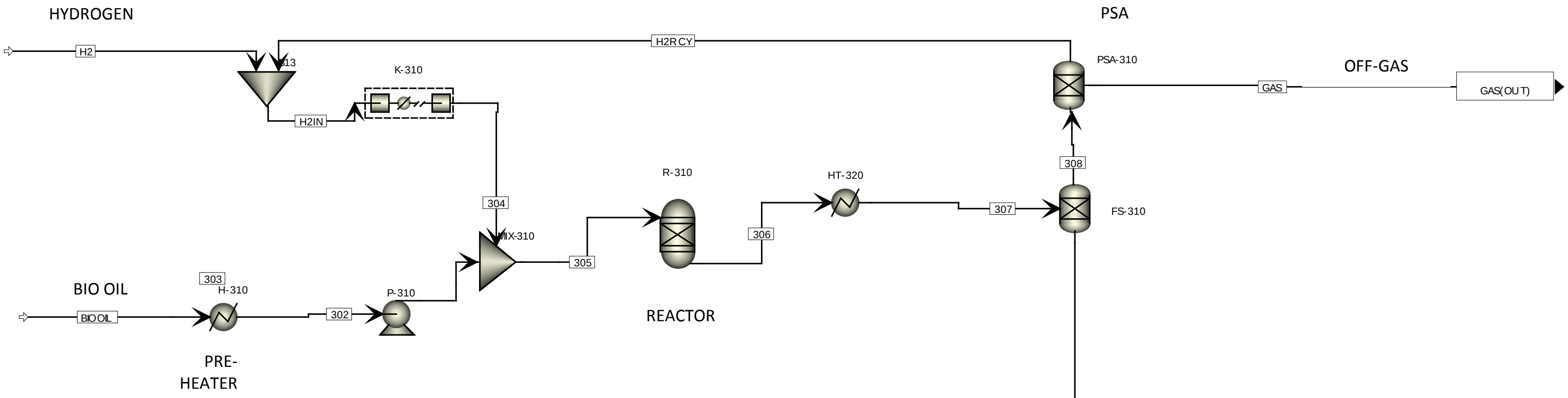
7.2 Fast Pyrolysis



	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

7.3 Fast pyrolysis bio-oil stabilization



	BIOOIL	H2	H2IN	302	303	304	305	306	307	308	OIL	GAS	H2RCY
Temperature C	35	40	54.9	60	64.7	117.6	106.3	85	60	60	60	60	60
Pressure bar	1.013	29.2	29.2	0.184	100	137.413	100	100	99	99	99	99	99
Volume Flow cum/sec	0.003	0.003	0.008	0.003	0.003	0.002	0.005	0.009	0.009	0.005	0.004	0.003	0.004
Enthalpy Gcal/hr	-28.054	0.001	0.007	-27.834	-27.793	0.021	-27.772	-27.566	-27.841	-0.873	-26.975	-0.88	0.012
Mass Flow kg/hr	**14952.3**	**21**	**62.2**	**14952.3**	**14952.3**	**62.2**	**15014.5**	**15014.5**	**15014.5**	**926.319**	**14088.18**	**885.119**	**41.2**
C2H4O-01	398.416			398.416	398.416		398.416	466.051	466.051		466.051		
C2H6O-01	19.215			19.215	19.215		19.215	19.004	19.004		19.004		
C3H6O-01	431.428			431.428	431.428		431.428	401.307	401.307		401.307		
C2H4O-02	1295.873			1295.873	1295.873		1295.873	1886.775	1886.775		1886.775		
C7H8O-01	1702.285			1702.285	1702.285		1702.285	3373.237	3373.237		3373.237		
C5H4O-01	399.125			399.125	399.125		399.125	621.36	621.36		621.36		
LEVOGLUC	4114.329			4114.329	4114.329		4114.329	127.635	127.635		127.635		
CO2								26.29	26.29	26.29		26.29	
CH4								267.55	267.55	267.55		267.55	
H2O	4285.093			4285.093	4285.093		4285.093	5142.171	5142.171		5142.171		
CO								563.149	563.149	563.149		563.149	
H2		21	62.2			62.2	62.2	51.5	51.5	51.5		10.3	41.2
C2H6-02								8.801	8.801	8.801		8.801	
C2H4-02								9.028	9.028	9.028		9.028	
C18H3-01	1276.9			1276.9	1276.9		1276.9	52.177	52.177		52.177		
C4H10-01	16.547			16.547	16.547		16.547	16.547	16.547		16.547		
C4H7N-01	303.804			303.804	303.804		303.804	303.806	303.806		303.806		
PYROLIGN	709.285			709.285	709.285		709.285	1678.11	1678.11		1678.11		

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

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