Mild Biomass Liquefaction Process for Economic Production of Stabilized Refinery-Ready Bio-oil

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Executive Summary

Southern Research (SR) in cooperation with U.S. Department of Energy (DOE), Bioenergy Technology Office (BETO), investigated a biomass liquefaction process for economic production of stabilized refinery-ready bio-oil. The project was awarded by DOE under a Funding Opportunity Announcement (DE-FOA-0000686) for Bio-oil Stabilization and Commoditization that intended to evaluate the feasibility of using bio-oil as a potential feedstock in an existing petroleum refinery. SR investigated Topic Area 1 of the FOA at Technology Readiness Level 2-3 to develop thermochemical liquefaction technologies for producing a bio-oil feedstock from high-impact biomass that can be utilized within a petroleum refinery.

Bio-oil obtained from fast pyrolysis of biomass is a green intermediate that can be further upgraded into a biofuel for blending in a petroleum refinery using a hydro-deoxygenation (HDO) route. Co-processing pyrolysis bio-oil in a petroleum refinery is an attractive approach to leverage the refinery's existing capital. However, the petroleum industry is reluctant to accept pyrolysis bio-oil because of a lack of a standard definition for an acceptable bio-oil feedstock in existing refinery processes. Also per BETO's multiyear program plan, fast pyrolysis-based bio-fuel is presently not cost competitive with petroleum-based transportation fuels.

SR aims to develop and demonstrate a cost-effective low-severity thermal liquefaction and hydro-deoxygenation (HDO) process to convert woody biomass to stabilized bio-oils that can be directly blended with hydrotreater input streams in a petroleum refinery for production of gasoline and/or diesel range hydrocarbons. The specific project objectives are to demonstrate the processes at laboratory scale, characterize the bio-oil product and develop a plan in partnership with a refinery company to move the technology towards commercialization.

The overall technical approach employed in SR's liquefaction process involved: (1) stable bio-oil (~20% oxygen) production using a methanol/water co-solvent system under mild conditions; and (2) bio-oil HDO using commercial hydrotreating catalysts to produce a fuel intermediate that can be directly blended with petroleum hydrotreater feed. A preliminary techno-economic model was constructed for the liquefaction process and it was iteratively updated to guide the process development.

The liquefaction process used a combined methanol-water solvent that synergistically enhances wood conversion to bio-oil and the stability of the bio-oil produced. The process was developed and demonstrated at laboratory scale using a Parr reactor. The liquefaction conditions were optimized using a factorial experimental design. Methanol/water co-solvent system demonstrated significantly lower severity conditions to decompose woody biomass when compared to those employed in hydrothermal liquefaction. Under optimized temperature and pressure, over 90% of biomass was converted to bio-oil, aqueous organics, and gas products, and the bio-oil yield was close to 50%.

A solvent extraction method was developed to extract raw bio-oil for characterization. The bio-oil produced from optimized condition contained 20 to 25% oxygen, near zero water and low acid content (TAN<5 mgKOH/g). The bio-oil was viscous and did not flow at room-temperature. But, the bio-oil was found to be stable; the molecular weight of aged bio-oil did not increase

significantly during the long-term storage. A GC/MS analysis of the bio-oil revealed a complicated oil composition with absence of typical sugar degradation products, e.g. glycoaldehyde which explains the enhanced bio-oil stability. Overall, the bio-oil produced from SR's solvent liquefaction process had improved physicochemical properties when compared to pyrolysis oil, but it still needed HDO to attain properties required for blending with a refinery hydrotreater feed.

The raw bio-oil was found to contain heavy oil and light oil fractions based on the results from gel permeation chromatography analysis. A natural phase separation method was developed to separate the light bio-oil from liquefaction slurry using a filtration and direct methanol distillation approach. The overall light oil yield attained from the process was ~37% with ~22% oxygen.

Based on discussion with selected refinery companies, the light bio-oil needed further HDO to reduce its oxygen (<10% oxygen) to enable blending and co-processing in a petroleum hydrotreater. Three commercial HDO catalysts were employed for light bio-oil upgrading. The raw bio-oil was diluted with alcohol to reduce the viscosity and improve the catalyst stability. Approximately100 hrs of HDO testing was achieved with two of the catalyst candidates without plugging of the reactor indicating that coking may not be significant. The upgraded oil was found to contain low-oxygen (~1%) at low H_2 consumption (<0.03 g/g). A simulated distillation analysis revealed diesel range hydrocarbon carbon (C_{10}-C_{24}) present in the upgraded oil. In addition, the upgraded oil was soluble in petroleum products, e.g. diesel, and thus it could be directly blended with petroleum feed for refinery.

A commercial embodiment that consisted of biomass solvent liquefaction and bio-oil HDO was developed using Aspen Plus simulation. A techno-economic analysis (TEA) and a life cycle assessment (LCA) were conducted by Dr. Eric Larson at Princeton University. The preliminary TEA and LCA results indicated that SR's process could produce finished fuel at $3.60/gallon using current state of technology and the cost can be further reduced to $2.80/gallon in the n^{th} plant design via several technical improvements. Environmentally, the process could reduce greenhouse gas (GHG) emissions by ~25% when compared to petroleum-based fuel emissions.

In summary, the novel biomass liquefaction process demonstrated a lab-scale prototype system to convert woody biomass to a potential fuel intermediate that could be acceptable in existing refineries. The technology developed in this project needs to be further verified and demonstrated at pilot-scale to attract interest from petroleum refineries. Additionally, the process needs further technical improvements using process optimization to increase light oil yield and to produce renewable hydrocarbon fuel at costs that are economically competitive with petroleum-based fuels.

1. Introduction

The objectives of this project are to (i) demonstrate a cost-effective low-severity thermal liquefaction and HDO process at laboratory scale to convert woody biomass to stabilized bio-oils that can be directly blended with hydrotreater and hydrocracker input streams and (ii) develop a plan in partnership with a refinery to move the technology towards commercialization. The long term goal is to demonstrate and commercialize the process at a petroleum refinery for production of gasoline and diesel range hydrocarbons.

The main technical approach used in this project was to utilize a unique solvent system, methanol and water, to effectively decompose woody biomass constituents into bio-oil. Parametric study was conducted to optimize the liquefaction conditions to achieve high bio-oil yield and quality. Several key physicochemical properties (e.g. oxygen content) of raw bio-oil were characterized for petroleum refineries to evaluate its suitability for co-processing. A continuous HDO step was developed to enhance the bio-oil acceptability in refinery via significant reduction of bio-oil oxygen-content. TEA and LCA analysis were iteratively updated to guide the process development.

Major project accomplishments are listed below:

1. Biomass solvent liquefaction was developed and demonstrated at the lab-scale to produce stabilized bio-oil. 90% biomass conversion to non-solids and ~55% bio-oil yield (~37% light oil yield) were achieved under optimized conditions.
2. Bio-oil physicochemical properties, stability and chemical composition were characterized to understand its suitability in refinery process.
3. In collaboration with a catalyst company, bio-oil was upgraded into a low-oxygen content hydrocarbon fuel intermediate using mild temperature and low H_2 consumption. The upgraded oil has good potential to be co-processed with crude oil distillates due to its superior physicochemical properties.
4. A commercial embodiment of biomass liquefaction process has been developed and verified with Aspen Plus Simulation. TEA & LCA analyses indicate that the proposed process could produce final fuel product at $3.60/gallon and reduce greenhouse gas emission by 25% when compared to petroleum baseline.
5. Discussions with refinery and catalyst companies identified technical challenges, e.g. bio-oil oxygen content and miscibility with petroleum feed that have been addressed with effective catalytic upgrading of raw bio-oil.

The report is organized to summarize the results obtained for the major tasks allocated for this project. These tasks include: Task A. Batch Reactor Studies, Task B. Continuous Reactor Studies, Task C. Techno-Economic Analysis and Life Cycle Assessment, and Task D. Refinery Collaboration. The technical results are presented in this report and they were also provided as a Data Mining Report to the National Renewable Energy Laboratory (NREL).

2. Experimental

2.1 Materials

Pulverized mixed southern pine wood (~100 µm, Fig.1) was used as the raw material for the liquefaction study. Ultimate, proximate analysis and chemical composition of the wood material are summarized in Table 1. DI (deionized) water and methanol (ACS grade) were used as liquefaction solvent.

Figure 1. Pulverized mixed southern pine wood.

Table 1. Ultimate and proximate analysis of mixed southern pine.

Ultimate analysis (dry base)	**Southern pine**
C, %	53.3
H, %	6.3
N, %	0.27
O, %	40.2
S, %	0.01
Proximate analysis	
moisture, %	10.2
volatile matter, %	72.6
fixed carbon, %	16.6
ash, %	0.63
Chemical composition	
glucan, %	44.8
xylan, %	3.0
galactan, %	1.3
arabinan, %	0.0
mannan, %	11.4
lignin, %	28.4
extractives, %	3.3

2.2 Methods

Biomass Liquefaction. In a typical liquefaction experiment, ~20-30g dry wood powders were mixed with the liquefaction solvent (methanol and DI water mixture) in a high-pressure Parr-reactor (Fig. 2). The reactor was then sealed and purged with nitrogen for 20 mins to replace the remaining oxygen in the reactor vessel. The reactor was then pressurized to 20 psig with nitrogen and heated up to a desired temperature. After maintaining the liquefaction temperature for a certain length of time, the reactor was quickly cooled to 30 °C using cold-water. Before opening the reactor, the gaseous products were collected into a pre-vacuumed gas-sampling bag and the gas composition was analyzed by a micro-GC (INFICON). The total mole amount of gas products was calculated by the ideal gas law and the void space of the reactor.

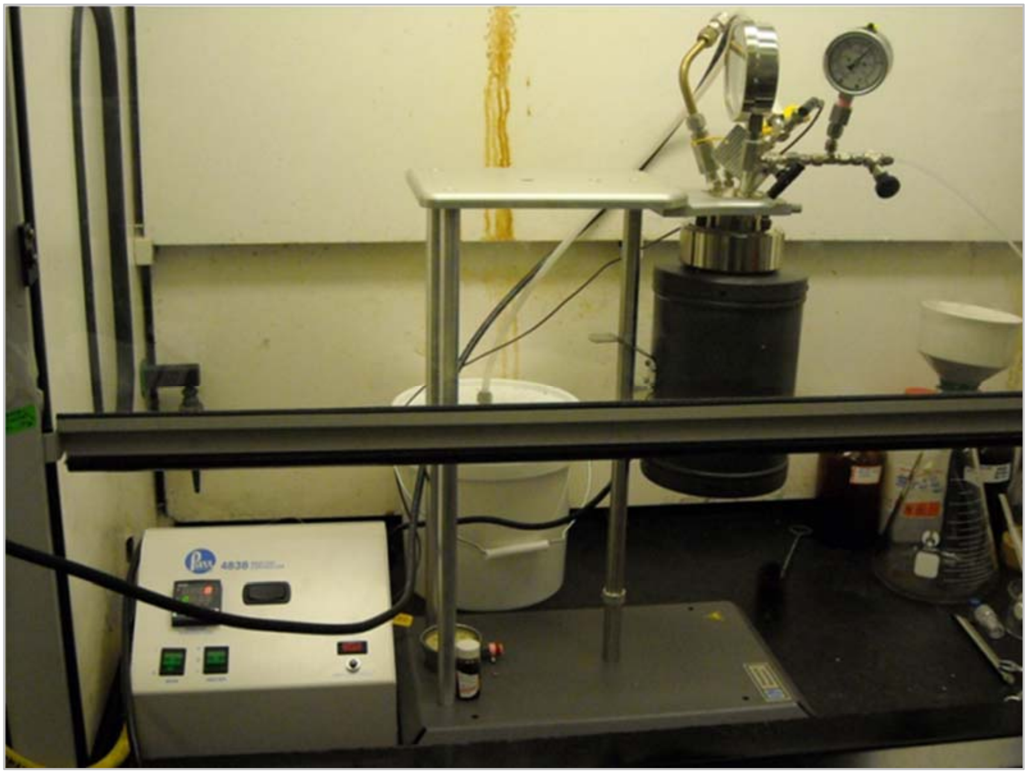

Figure 2. Parr reactor used for biomass liquefaction.

Liquefaction Product Separation using Solvent Extraction. A sample extraction/separation method (Fig. 3) was developed to separate reaction products for analysis. Following a liquefaction run, the reactant slurry is first filtrated using a pre-weighted filter paper (Whatman No.1) and the collected solids were rinsed with 100 ml of organic solvent (propyl acetate and butyl acetate mixture, $V_{\text{propyl acetate}}:V_{\text{butyl acetate}} = 3:1$) to ensure maximum recovery of bio-oil into the liquid phase. This particular solvent (referred as solvent A) was also used for bio-oil extraction and the extracted oil can be found in Fig.4. The collected solids were dried in a convection oven at 105 °C for 4 hours before weighting. After removing the solids, the liquid phase was extracted with equal amount of solvent A (volume ratio at 1:1) in a separatory funnel to separate the bio-oil from the aqueous phase. The organic layer containing solvent A and methanol was then vacuum dried under 60 °C and the residue viscous liquid is referred as bio-oil in this study. The collected bio-oil and the aqueous phase were weighted and stored in a refrigerator (4 °C) for further analysis.

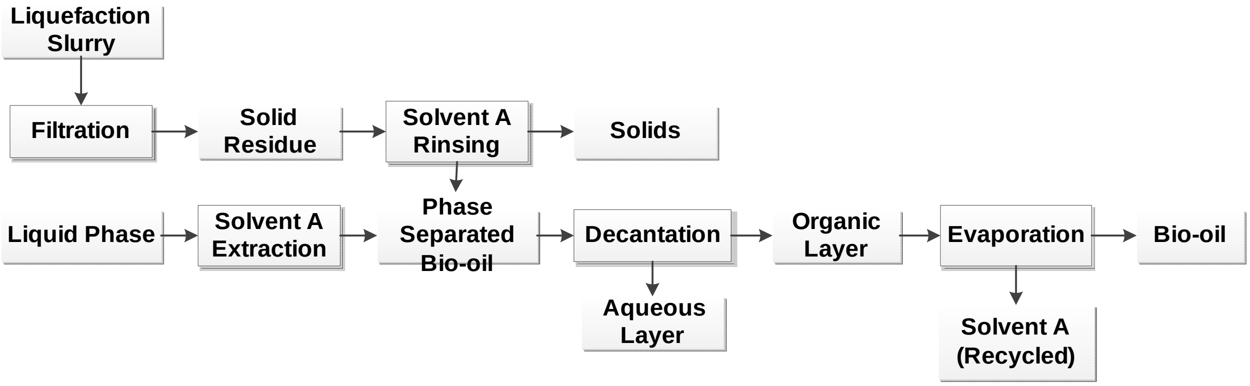

Figure 3. Liquefaction product separation procedure using solvent extraction.

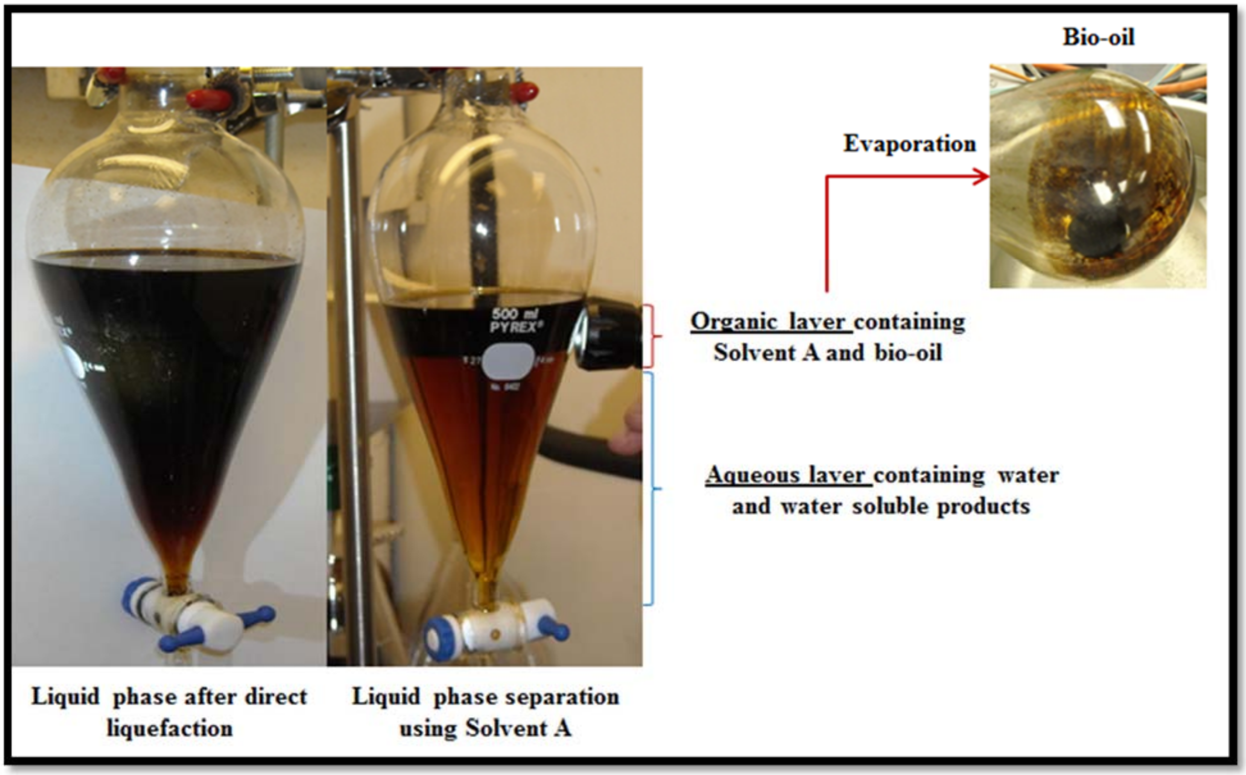

Figure 4. (a) Liquefaction contents immediately after reaction; (b) Overnight separation of aqueous and organic phase of the bio-oil using solvent A; (c) Rotary evaporation of the nearly pure bio-oil product.

Liquefaction Product Separation using Direct Methanol Evaporation. Solvent A based bio-oil extraction process has no scale-up potential due to excess use of organic solvents, potential solvent loss and expensive solvent recovery process, e.g. vacuum distillation. In addition, solvent A was found to extract heavy bio-oil fraction that is not suitable for further upgrading to transportation fuel. For the commercial embodiment, a new bio-oil separation process (Fig. 5) was developed to recover the bio-oil with low molecular weight for further upgrading. As most bio-oil components are hydrophobic, direct evaporation of methanol in the liquefaction product slurry was expected to achieve the similar phase separation as when solvent A was used. As shown in Fig. 5, the liquefaction slurry was first filtered to separate the solid residue. The liquid filtrate was vacuum-evaporated to recover liquefaction solvents. When gradually evaporating methanol, a reddish aqueous phase was formed and the viscous bio-oil droplets precipitated on the evaporation flask. The bio-oil was then collected by decanting the aqueous phase. This bio-oil is defined as methanol soluble (MS) bio-oil. In addition to bio-oil solubilized in liquefaction solvent, a significant amount of bio-oil (heavy fraction) cohabited with the solid residues and they can be extracted with acetone for recovery. After evaporating the acetone, these bio-oils appeared to be in solid-gum shape and cannot be processed in the upgrading process. The heavy bio-oil was defined as acetone soluble (AS) oil.

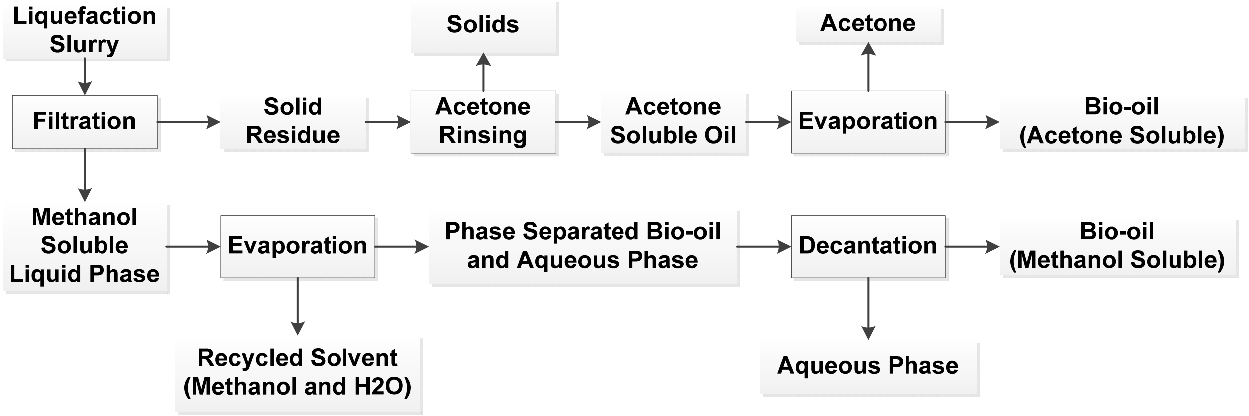

Figure 5. Methanol soluble (light) and acetone soluble (heavy) oil separation procedure.

Liquefaction Product Characterization. *Elemental Composition.* The carbon, nitrogen and hydrogen content of bio-oil were quantified using a Perkin Elmer CHN Elemental Analyzer (2400 Series II) according to ASTM D5291. The oxygen content was calculated by difference. *Water Content.* The bio-oil water content was determined by Karl-Fischer titration according to ASTM E 203-08 using HYDRANAL Composite 5 (Sigma-Aldrich 34805) by dissolving bio-oil in methanol or chloroform. The titrant concentration was determined by HYDRANAL Water Standard 10.0 (Sigma-Aldrich 34849). *Viscosity.* The liquefaction bio-oil collected in this study looked very similar to plasticine in terms of high viscosity and it did not flow at room-temperature. Direct viscosity measurement on its raw state using capillary or Brookfield viscometer is not feasible. Therefore, the viscous bio-oil was diluted with DMSO solvent and measured with a Stabinger viscometer (Antor Paar, SVM 3000) at 40 °C. *Acidity.* The total acid number (TAN) of bio-oil was measured according to modified ASTM D644-07 with manual titration. The bio-oil was dissolved in acetone instead of toluene, isopropanol and water mixture. 0.1M KOH dissolved in isopropanol solution was prepared as titrant. Since, the titration curve did not show well-defined inflection point; buffer potential method (pH=7 buffer) was employed to determine the titration end point. The TAN numbers reported in this study represent the KOH consumption where the bio-oil solution was titrated to pH 7. *GC/MS Analysis*. Gas chromatographic/mass spectrometric analyses of the bio-oil were performed on a Shimadzu GC/MS-AP2010. The MS detector was set at a full scan mode with a mass to charge range from 10 to 550 amu. Standard electron impact (EI) ionization at 70ev was employed and the ion source temperature was set up at 200°C. The GC column used for separation was a DB-5 column 60m × 0.25mm with 0.25μm film thickness. The GC oven temperature was initially held at 45°C for 4 mins, then ramped at 3 °C/min to 280°C, and held at 280°C for 15 mins. The injector and detector temperatures were set at 250°C and 280°C, respectively. The injector split ratio was fixed at 30:1. High purity helium was employed as the GC carrier gas at a flow rate of 38 cm/min, and the bio-oil sample was prepared as 6 wt% solutions dissolved in acetone pre-filtered with a 0.25 µm PTFE filter. 1 µL of bio-oil solutions were injected for each analysis and duplicated tests were performed for each analysis. The quantification of bio-oil components was achieved by searching NIST 2008 MS library. *GPC Analysis.* Gel Permeation Chromatography (GPC) characterization of the bio-oil was carried out on a HPLC system (Aglient 1100) equipped with an RI detector (RID-10A). Two columns (WatersStyragel HR-1 and HR-5E) are connected for the separation of bio-oil components. The column oven temperature was set at 35 ºC. Tetrahydrofuran (THF, Sigma 401757) was used as the mobile phase flowing at 0.7 mL/min. Bio-oil sample was dissolved in THF to approximately 2 w.t. % and then filtered through a 0.25 µm PTEF filter. Twelve polystyrene standards with molecular weight ranging from 162 to 3,520,000 were used to generate the calibration curve.

Bio-oil Hydrodeoxygenation (HDO) in Continuous Reactor. The hydrodeoxygenation experiments were carried out in a continuous trickle-bed reactor (OD: 1/2 inch) using catalysts provided by a commercial company. Before feeding bio-oil, the catalyst was properly activated according to the procedure suggested by the catalyst supplier. The MS oil was dissolved in alcohol and fed into a fixed-bed reactor using a high-pressure pump (Eldex, 1SM) along with H_2 (5% Argon as internal standard). The offgas composition was analyzed using a micro-GC. The upgraded oil properties, including elemental composition, water content, GC composition, were characterized using the same analytical methods described for raw bio-oil.

3. Results and Discussion

3.1 Parametric Study of Biomass Liquefaction

Converting solid biomass into liquid bio-oil using supercritical water alone needs to heat water above 374 °C and maintain a high pressure around 3200 psig. The harsh reaction conditions which adversely affect the process economics could be improved by using water-methanol mixture as process solvent, because supercritical methanol can be generated in less severe conditions (approximately 240 °C and 1200 psig). In addition, while subcritical water mainly acts like a hydrolysis reagent for biomass degradation, supercritical methanol provides better dissolution power when compared to water, therefore increase the overall conversion of biomass under this hybrid solvent system.

To investigate the optimal reaction conditions for this novel solvent system, a statistical ¼ factorial design on four reaction parameters (liquid to wood ratio-L/W, temperature, reaction time, and water to methanol ratio-W/M) were employed. Different from the traditional One-Variable-At-a-Time experimental design, which is unreliable and time-consuming, the experimental design employed in this study ensures a quick determination of the main factor which affects the process efficiency and product quality. In addition, other than obtaining a single-factor effect, the effect of interactions between different factors can also be evaluated. After obtaining the main factors which critically affect the liquefaction, the optimal conditions will be chosen to obtain over 90% biomass conversion, 50% bio-oil recovery and <25% oxygen content in bio-oil with the least severe reaction conditions.

Table 2 provides the experimental results using statistically designed conditions. Overall, the biomass conversion and bio-oil yield ranged from 50-94% and 23-59.8% respectively and the bio-oil oxygen content falls in a range between 26.1 to 33%.

The Pareto plots, shown in Fig. 6 determine the main factors and interaction effects that are most important to the process outcomes. From the plots, it is determined that the biomass conversion is dominated by four single process factors and two interactions effects (L/W and temperature, L/W and W/M). Among them the reaction temperature is the most critical one and it also determines the oxygen content in the bio-oil. Similar to biomass conversion, bio-oil yield is also affected by the four individual factors and two interaction effects (L/W and temperature, L/W and W/M). However, the interaction between temperature and W/L rather than a single factor had the most significant effect.

Table 2. Summary results of ¼ factorial design of experiments

Runs	Biomass conversion, %	Bio-oil yield, %[b]	Bio-oil oxygen content, %
1, 5	50.0	32.5	31.3
12, 13	68.8	43.8	27.7
2, 3	52.7	32.3	33.0
8, 10	51.4	23.0	27.9
7, 9	90.0	51.9	28.1
16, 17	76.8	24.1	25.7
6, 11	86.1	35.0	26.1
4, 15	87.4	39.0	26.1
14, 18	94.0	59.8	26.3
19, 20[a]	91.0	51.2	26.8

a. Experimental conducted under optimal conditions
b. Bio-oil recovered using solvent A

Base on the experimental results and also considering commercial production feasibility, the optimal liquefaction conditions for achieving high biomass conversion and bio-oil yield with moderate oxygen content was determined. The verification results of the liquefaction conditions were summarized in Table 2 (run 19 and 20). When the liquefaction was performed under the optimal conditions, over 90% of solid wood can be converted and close to 50% can be extracted as bio-oil (MS+AS oil) which contains moderate amount of oxygen of 26.1%. These results meet the predefined targets.

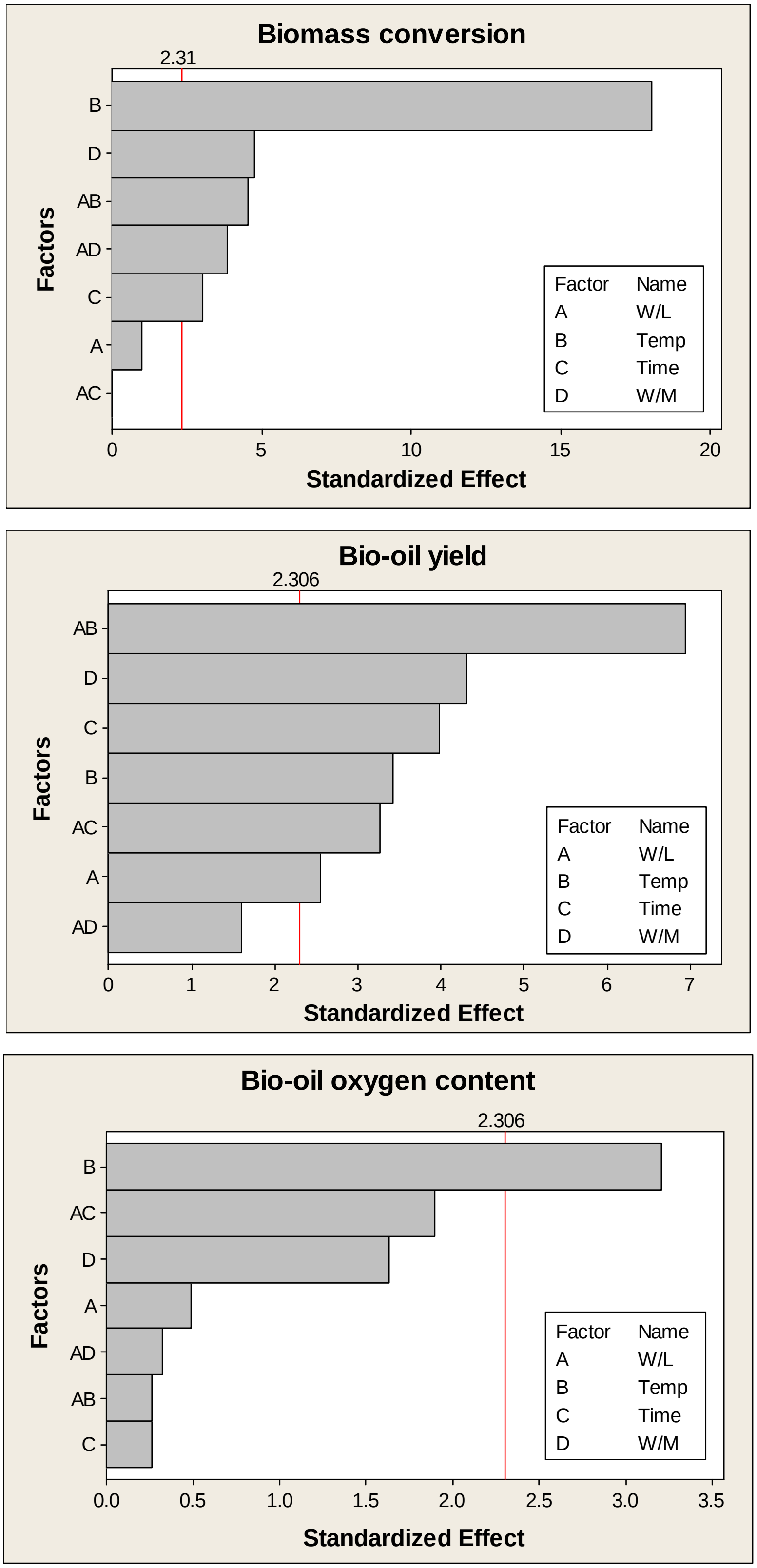

Figure 6. Pareto chart of the standardized effects (α=0.05) on biomass conversion, bio-oil yield and bio-oil oxygen. The factor is potentially significant if its standardized effects extend over the reference line (red).

3.2 Mass and Elemental Balance of Biomass Liquefaction under Optimized Conditions

The mass balance of liquefaction performed under optimized conditions was summarized in Table 3. After liquefaction, approximately 50% of wood can be converted to bio-oil; 35.7% of liquefied wood dissolved in water as aqueous phase; ~9% of wood cannot be converted and remained as a solid. It is also worth to point that the solid residue could result from re-polymerization of primary liquefaction products, not solely from the unreacted wood. Due to the mild reaction conditions, the process did not generate significant amount of gas products (<5%, CO_2 rich), indicating decarboxylation is not the primary reaction for this process. In addition, Table 3 also presents the elemental balance of the liquefaction experiment. The carbon and hydrogen were preferentially accommodated by bio-oil followed by aqueous phase, solid residues and gas. The oxygen, however, was mostly transformed into liquid products as 57% went to aqueous phase and 30.7% went to bio-oil; the solid residue and gas carried significantly lower amount of oxygen than the liquid products.

Table 3. Mass and elemental balance of liquefaction process (based on dry wood).

	Bio-oil	Aqueous Phase[a]	Solid Residue	Gas[b]
Mass distribution, %	50.8	35.7	9.3	4.2
Elemental Distribution				
C, %	66.5	18.4	12.4	2.7
O, %[a]	30.7	57.0	5.8	6.5
H, %	61.3	28.9	9.0	0.8

a. Calculated by difference
b. Calculated by ideal gas law and micro-GC gas composition

These results indicate that the bio-oil and aqueous phase are major reaction products from solvent liquefaction of woody biomass. Although, in this process, bio-oil is of primary interest for fuel production, effective use of the second largest products, aqueous phase will be beneficial to the overall process economics and it may be achieved by producing specialty chemicals, e.g. sugar derivatives, using catalytic reforming or producing renewable H_2 using hydrothermal gasification process. Moreover, the distinct elemental distribution makes liquefaction a competitive process for fuel intermediate production as fuel-desired elements, carbon and hydrogen, were preferentially transferred into bio-oil while the oxygen was largely converted into aqueous phase.

3.3 Bio-oil Physicochemical Properties and Chemical Composition

The project attempts to produce bio-oil with improved physicochemical properties when compared with pyrolysis oil. Specifically, the liquefaction bio-oil are desired to have low oxygen content, low water content and low TAN number while the viscosity or molecular weight change over a long storage time indicating the stability, needs to be minimized.

Table 4 summarizes the physicochemical properties of liquefaction oil made from the optimized process. As shown, the liquefaction oil contains ~25% oxygen, much lower than pyrolysis oil (~40%); the water content and TAN number are also low. These characteristics indicate that liquefaction bio-oil could be a good fuel intermediate for downstream upgrading. The low oxygen content would require less hydrogen for hydrodeoxygenation; the low water content increase the oil heating value and the low acidity could inhibit the bio-oil condensation improving its storage stability.

A longstanding issue with liquefaction bio-oil is its high viscosity beyond measurement using conventional technique. In this project, the bio-oil viscosity was not measured directly using viscometer due to the lack of flowability but it can be reflected by its average molecular weight. As clearly presented in Table 5, both Mw and Mn of liquefaction oil are significantly high. The bio-oil (MS and AS combined) does not flow at room-temperature. The viscous nature of liquefaction oil implies that it needs to be dissolved in solvents or co-processed with low viscosity feedstock in the upgrading step.

Table 4. Physicochemical properties of liquefaction oil.

		Liquefaction oil[a]
Elemental Composition	C, %	65.4
	H, %	7.0
	O, %	26.8
	N, %	0.13
Physicochemical Properties	Water Content, %	2.5
	TAN, mg KOH/g	1.4
	Mw, g/mol	1605
	Mn, g/mol	925

a. Recovered using Solvent A extraction process.

When dissolving the liquefaction oil (obtained from solvent A extraction) in alcohols, we found the bio-oil was only partially soluble. The upgrading process however, requires bio-oil to be dissolved in alcohol for viscosity reduction and enhancement of upgrading performance. Using the direct methanol evaporation method, the whole bio-oil is separated into light methanol soluble (MS) and heavy acetone soluble (AS) oil. Their characteristics are summarized in Table 5. It is found that the AS oil had much lower oxygen content but higher molecular weight than the light oil. The AS oil is potentially a mixture of unreacted wood constituents and polymerized primary liquefaction products. Since it has low solubility in alcohol based solvent, it is not considered as a suitable feed for HDO upgrading.

Table 5. Physicochemical properties of light and heavy liquefaction oil.

		MS oil	AS oil
Elemental Composition	C, %	67.2	81.4
	H, %	6.9	3.9
	O, %	25.7	14.3
	N, %	0.20	0.40
Physicochemical Properties	Water Content, %	7.6	5.5
	TAN, mg KOH/g	1-3	1-3
	Mw, g/mol	1022	1762
	Mn, g/mol	592	1141

The chemical composition of bio-oil obtained from solvent A extraction and direct methanol evaporation method is characterized by GC/MS and listed in Table 6. The bio-oil was found to contain very complicated chemical compounds and only ~60% of the total peaks can be identified by the standard GC library. Methyl esters were found in the bio-oil indicating methanol may have participated in the liquefaction reaction reacting with the acid components in the bio-oil.

Table 6. GC/MS characterization of bio-oils made from optimum liquefaction using solvent A extraction and direct methanol evaporation.

Bio-oil chemical compounds	Solvent A Extraction	Direct methanol evaporation
Methyl Alcohol	10.6%	3.5%
Acetone	0.6%	11.1%
Ethanone, 1-[4-(methyltelluro)phenyl]-	0.8%	1.4%
Furan, tetrahydro-2-methyl-	1.0%	1.6%
2-Propanone, 1-hydroxy-	2.2%	2.0%
n-Propyl acetate	1.1%	0.6%
Furan, tetrahydro-2,4-dimethyl-, trans-	0.2%	0.9%
Butane, 1,1,3-trimethoxy-	1.4%	1.0%
1-Propanol, 2-methoxy-	0.5%	1.2%
Acetic acid, butyl ester	22.0%	0.3%
Furfural	1.6%	1.6%
2-Propanol, 1-ethoxy-	2.4%	1.3%
2-Furancarboxaldehyde, 5-methyl-	0.4%	0.8%
Pentanoic acid, 4-oxo-, methyl ester	1.3%	0.7%
2-Furanmethanol, tetrahydro-	0.6%	0.4%
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	1.6%	0.7%
Acetic acid, heptyl ester	0.7%	0.5%
Guaiacol	1.2%	1.0%
2-Cyclopenten-1-one, 3-ethyl-2-hydroxy-	0.6%	0.4%
Hepta-2,4-dienoic acid, methyl ester	0.8%	0.5%
Cyclopropanecarboxylic acid, 2-pentyl-, methyl ester	0.7%	0.3%
Catechol	1.3%	0.7%
5-Hydroxymethylfurfural	1.5%	0.7%
2(3H)-Furanone, 5-hexyldihydro-4-methyl-, (4R-cis)-	0.7%	0.1%
Phenol, 4-ethyl-2-methoxy-	1.2%	1.1%
Vanillin	0.9%	0.9%
trans-Isoeugenol	1.0%	1.2%
Nonanedioic acid, dimethyl ester	0.7%	0.9%
Methyl-(2-hydoxy-3-ethoxy-benzyl)ether	0.7%	0.9%
5-(7a-Isopropenyl-4,5-dimethyl-octahydroinden-4-yl)-3-methyl-pent-2-en-1-ol	0.5%	1.3%
Hexadecanoic acid, methyl ester	0.5%	1.4%
Phenol, 4-[2,3-dihydro-7-methoxy-3-methyl-5-(1-propenyl)-2-benzofuranyl]-2-methoxy-	0.5%	1.5%
6-Octadecenoic acid, methyl ester, (Z)-	3.2%	9.9%

Table 6 Continue.

9,12-Octadecadienoic acid, methyl ester	0.2%	1.5%
Methyl 5,11,14-eicosatrienoate	0.3%	1.0%
5-Androstene-3.beta.,7.beta.-diol 3-isocaproate	0.1%	1.9%
Total	65.0%	56.8%

3.4 Bio-oil Stability

The storage stability of liquefaction bio-oils was investigated by monitoring its viscosity and average molecular weight change during reservation. The results obtained from bio-oil aging tests indicate that the liquefaction bio-oil is substantially stable during the long-term storage. As shown in Fig. 7, four bio-oil samples previously obtained from optimization experiments showed consistent viscosity during the first three month storage; after that, the bio-oils, e.g. Day 20, showed approximately 10% viscosity increase indicating potential polymerization may have occurred. Compared to typical pyrolysis oil, which shows quick viscosity increase in the first three month storage, these liquefaction bio-oils are considered to be stable.

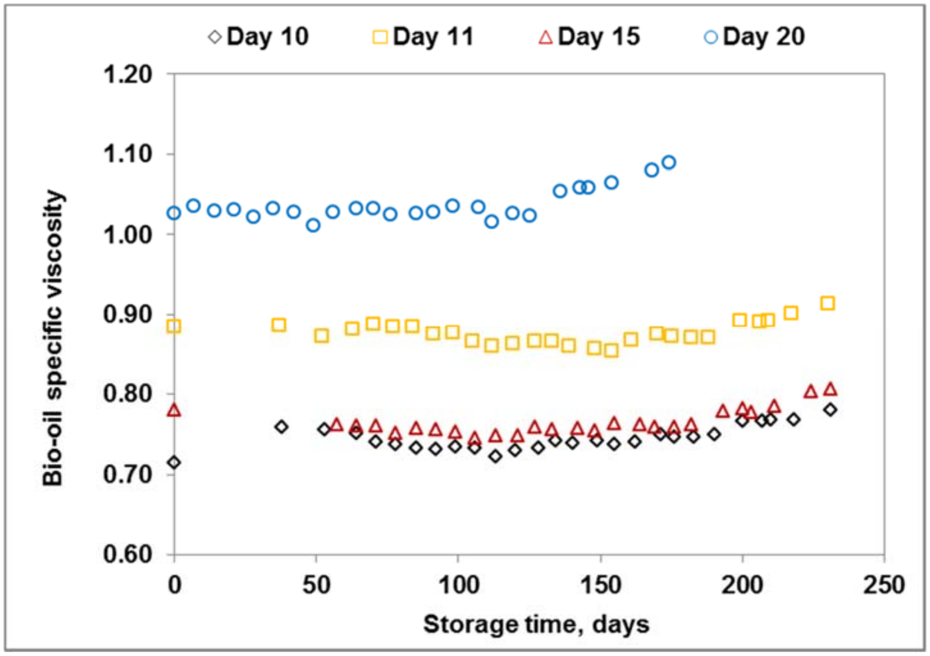

Figure 7. Bio-oil (solvent A extracted) viscosity change during storage.

The stable nature of liquefaction bio-oil can be tied to two aspects. First, most organic acids derived from carbohydrate decomposition have been migrated into the aqueous phase which renders the bio-oil with very low acidity, similar to crude oil (~1 mg KOH/g). As bio-oil condensation is catalyzed by those organic acids, bio-oil with low TAN value provides unfavorable reaction environment for acid-catalyzed polymerization. In addition, the low water content also renders the liquefaction bio-oil to be stable. If bio-oil contains significantly amount of water, e.g. 30%, its heavy lignin fraction tends to form aggregates and slowly separate out from the aqueous phase leading to phase separation and viscosity increase. However, with <1% water in the liquefaction bio-oil, such physical phase aggregation and separation is less likely to occur.

As the bio-oil viscosity was indirectly measured by dissolving in DMSO, its reliability on reflecting bio-oil stability is uncertain, because solvent may affect the bio-oil viscosity results. Another approach to studying bio-oil stability can be performed by measuring the bio-oil molecular weight change. Fig. 8 plotted the Mw and Mn change for the Day 20 bio-oil sample (performed under optimal conditions) during the six month storage. In addition, the corresponding viscosity change is also included in the plot for comparison. Similar to the conclusion drawn from viscosity change, the bio-oil molecular weight did not vary significantly during the storage. Both Mw and Mn had ~10% increase during the first one month storage and then it starts to level off. This confirms the stable nature of liquefaction bio-oil.

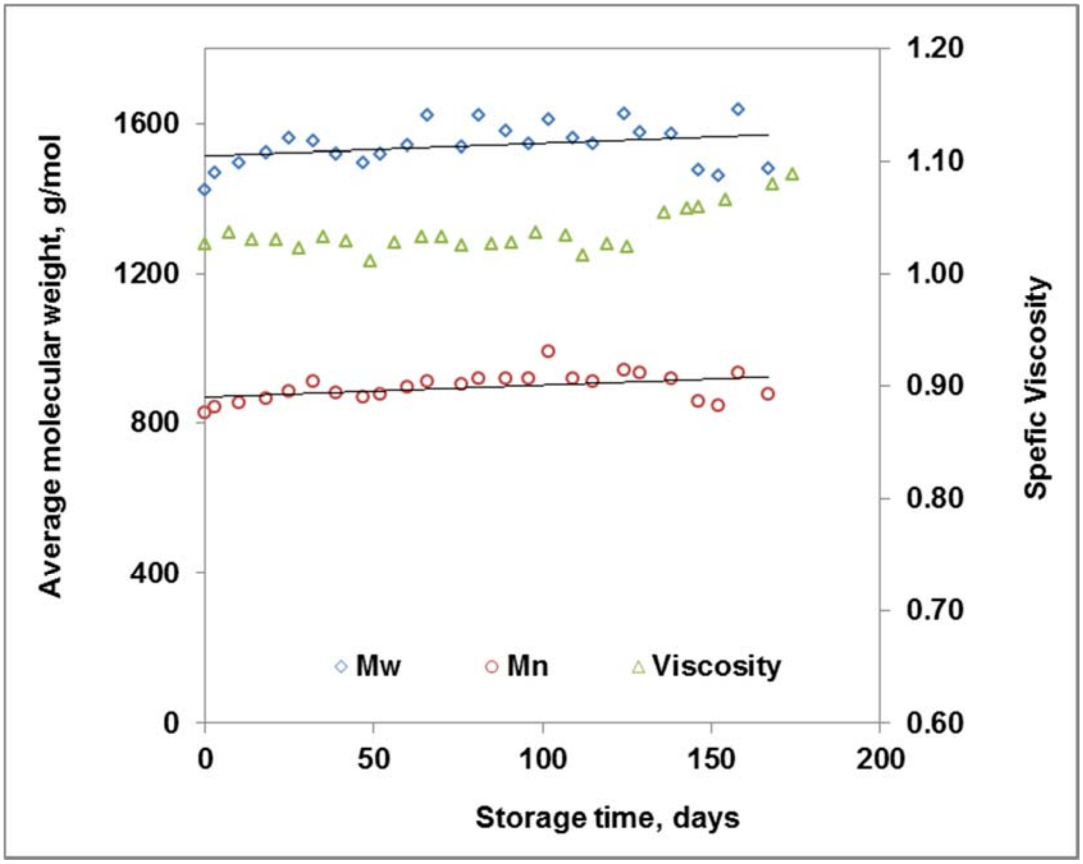

Figure 8. Bio-oil (Day20, Solvent A extracted) average molecular weight change during storage.

The stability of MS and AS oil presented as the molecular weight change over storage time is shown in Fig. 9. Similar to the whole bio-oil extracted using solvent A, the molecular weight change of these two oil fractions are very minor over two month storage and this suggests that separated bio-oil fractions are also stable.

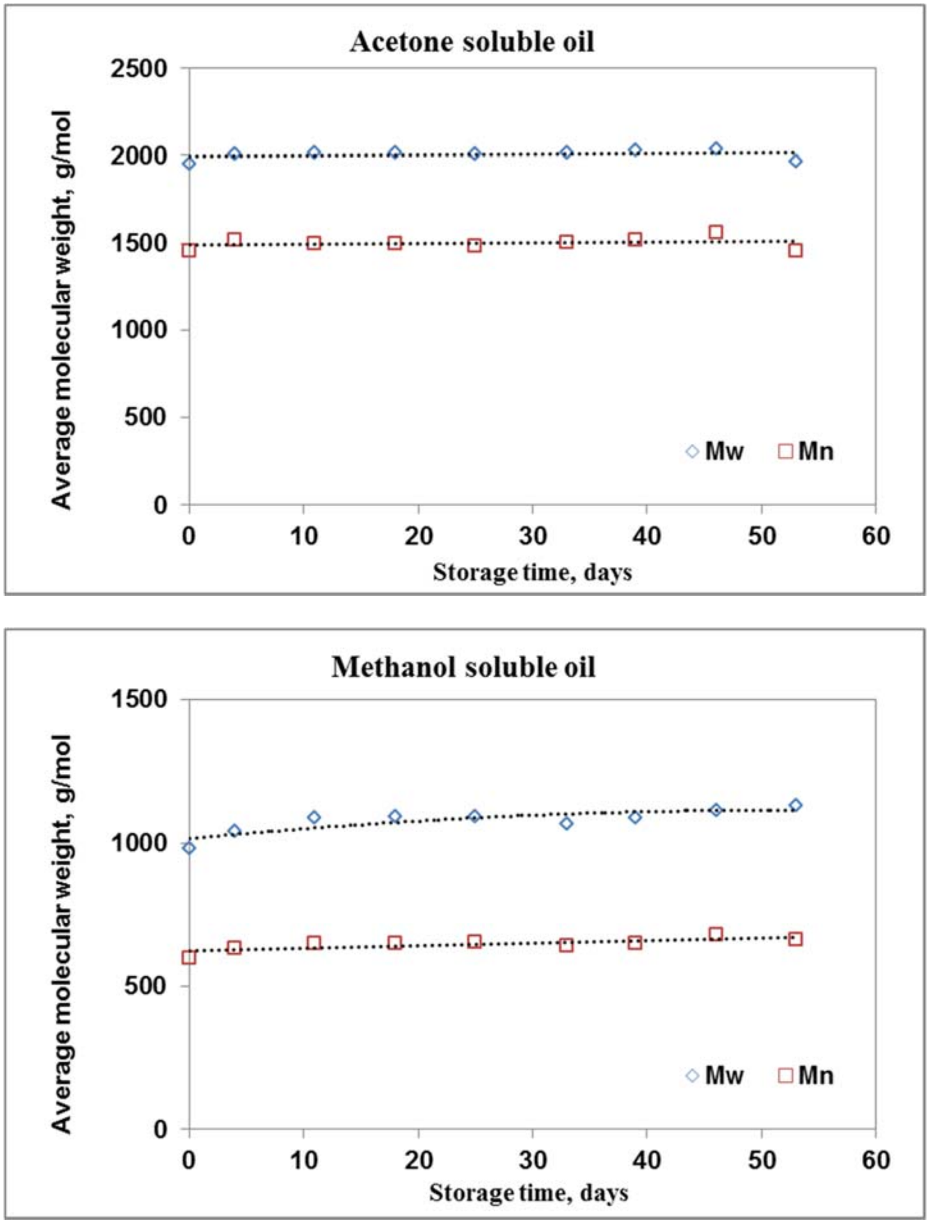

Figure 9. MS and AS oil (direct methanol evaporation method obtained) average molecular weight change during storage.

In addition to storage stability, the bio-oil thermal stability was evaluated by heating the bio-oil at 80 °C for 24 hours in a convection oven. As liquefaction bio-oil may be preheated at low temperature before entering the hydrotreater, good thermal stability is essential to prevent coke formation in the preheating pipeline and the hydrotreating reactor.

At 80 °C heat treatment, the viscous bio-oil was found to melt and flow slowly in a sealed glass tube. This indicates that liquefaction bio-oil could flow upon low temperature heating. When comparing the bio-oil molecular weight, it was found the combined MS and AS bio-oil had negligible molecular increase as shown in Table 7. These results suggest that liquefaction oil has a good thermal stability when heated for transportation purpose.

Table 7. Bio-oil (MS+AS) molecular weight change after accelerated aging.

	Fresh bio-oil	Heated bio-oil	Mw change, %
MS+AS oil			
Mw, g/mol	1621	1687	4.1
Mn, g/mol	986	1046	6.0

4. Continuous Bio-oil Hydrodeoxygenation

A continuous trickle-bed hydrotreator was designed and manufactured at SR for bio-oil hydrotreating study. ~20 g of hydrotreating catalysts was loaded into a fixed-bed reactor and they were activated with diesel/DMDS solution. Bio-oil dissolved in alcohol was continuously injected into the tube reactor for a minimum of 48 hours under designated hydrotreating conditions and the upgraded oil solution was condensed and collected for analysis. The diluent when blended with bio-oil was expected to facilitate the bio-oil hydrodeoxygenation and also serve as a heat sink for highly exothermic reaction.

As shown in Fig. 10, when bio-oil was dissolved in the alcohol, it appeared to be a dark-brown solution. After hydrodeoxygenation, the bio-oil solution became clear and separated into two layers. The bottom layer contains significant amount of water and the top layer consists of the solvent and upgraded oils (Table 8). Organic oil loss to aqueous phase was low at 0.5%.

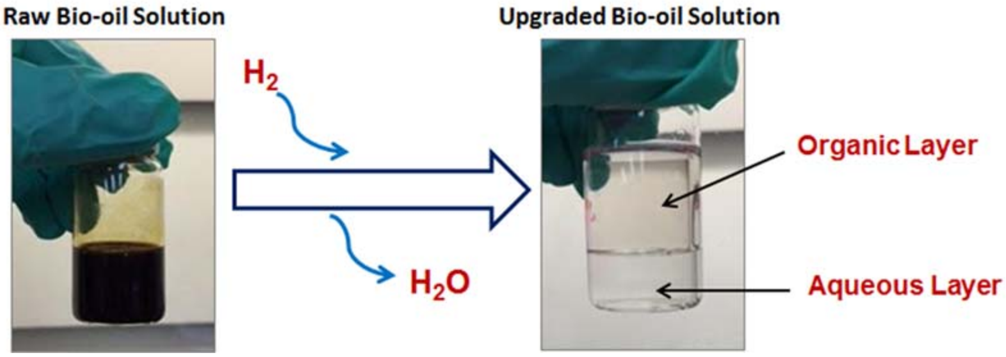

Figure 10. Appearance of bio-oil solution in isobutanol before and after hydrotreating.

Table 8. Chemical composition of upgraded oil.

	Alcohol, %	H_2O, %	Oil, %
Top layer	72.7	10.7	16.6
Bottom Layer	12.7	86.8	0.5

The HDO mass balance is summarized in Table 9. The hydrotreating gave ~75% oil and 85% carbon yield. The coke yield is low compared to the typical upgrading of pyrolysis oil (~20%). ~20% water was generated after hydrotreating. The hydrotreating tail gas consists of H_2, methane, and carbon dioxide. Based on dry oil input, methane and carbon dioxide as main gas products from bio-oil upgrading were less than 5%. The low carbon loss to gas phase and coke explains why a high carbon recovery is achieved into upgraded oil. Additionally, the consumption of molecular hydrogen (0.023 g/g dry oil) during bio-oil hydrodeoxygantion is also significantly lower than the pyrolysis oil (0.04-0.06 g/g). The low H_2 consumption indicates minimized double bond saturation in bio-oil chemical components during the HDO and it may be a result of the dilution effect.

Table 9. Mass balance of bio-oil hydrotreating.

	Yield, %
Upgraded Bio-oil[a]	73.7
Bio-oil Carbon[a]	85.4
Coke[a]	6.5
H_2O[b]	20.4
Gas[b,c]	3.5
H_2 consumption, g/g dry oil	0.023

a. Based on dry bio-oil input
b. Based on total feed of bio-oil/isobutanol solution
c. Gas composition consists of H_2, CH_4, CO_2

The elemental composition of upgraded oil was shown in Table 10. The bio-oil feed (dry base) had ~22% oxygen; after mild HDO treatment, it decreased to 1.5%. The upgraded oil with low oxygen content is expected to be partially recycled back to HDO process as the diluent and the rest of it can be directly blended with petroleum feed for further refining.

Table 10. Elemental composition of dry oil.

	Raw Oil	**HDO Oil**
C, wt%	70.6	85.1
H, wt%	7.0	13.4
N, wt%	0.27	N.D.
O[a], wt%	22.2	1.5

a. Oxygen was calculated by difference

The HDO oil solution was distillated to obtain concentrated oil sample removing alcohol diluent and H_2O for GC/MS quantification and blending test with petroleum feed, i.e. diesel. Fig. 11 shows the GC/MS spectrum of distillated HDO oil with carbon number identification. Hydrocarbon components with carbon number of C_{12} to C_{24} were observed in the distillated oil which makes this fuel precursor fallen in the diesel fuel range.

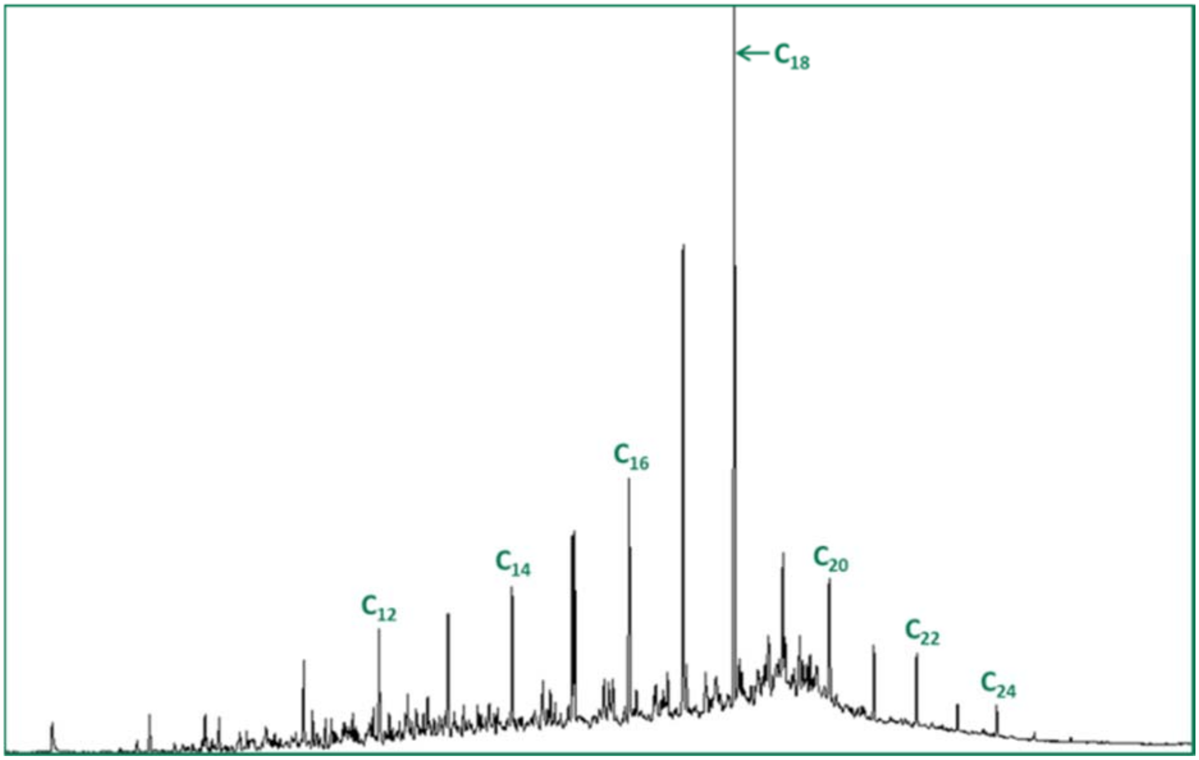

Figure 11. GC/MS characterization of distillated HDO oil.

The miscibility of distillated oil with petroleum diesel was also carried with 20 wt% HDO oil and 80 wt% diesel. Unlike raw bio-oil which is completely immiscible with diesel, the HDO oil immediately dissolved in the diesel after mixing. This facilitates the direct co-processing of bio-oil with petroleum feed. Due to insufficient amount of HDO oil available in the lab, miscibility test of HDO-oil with diesel at other ratios was not performed.

5. Preliminary TEA and LCA

Based on the lab results, a process model was constructed using Aspen Plus Simulation. The commercial process is composed of three major sections, biomass liquefaction, product separation and recovery, and bio-oil hydrotreating. TEA and LCA models were developed for estimating the cost of producing refinery-ready bio-oil and for estimating the net fuel-cycle greenhouse gas (GHG) emissions of the bio-oil. Baseline results are generated for both current state-of-the-art (SOT) production technology and for technology with future-target characteristics (TARGET). Key inputs to the cost and emissions models were based on experimental and process simulation work[1]. Inputs to the cost and emissions models include the composition and heating value of the input biomass (Table 11), which for cost and emissions modeling purposes, is assumed to come from Southern pine plantations, and steady-state mass and energy balances for the SOT and TARGET plant designs (**Error! Reference source not found.** 12). Modeling is carried for a commercial-scale plant processing 1,366 short tons per day of as-received biomass. The annual biomass requirements, assuming capacity factors of 90% for the TARGET plant and 75% for the SOT plant, are given in Table 13, along with annual quantities of the other required inputs and the annual output quantities of "HDO oil" (the final plant oil product) and ash.

Table 11. Biomass feedstock composition and heating value.

	As received	As fed
Proximate analysis (wt%)		
Moisture	0.265	0.102
Volatiles	0.601	0.726
Fixed carbon	0.131	0.166
Ash	0.003	0.006
HHV, btu/lb, dry	8,192	8,145
HHV, btu/lb	6,021	7,314
Ultimate analysis (wt% MAF)		
C	0.489	0.533
H	0.052	0.063
N	0	0.0027
O	0.465	0.402
HHV, btu/lb	7,752	8,370
HHV, kJ/kg	18,033	19,471
LHV, btu/lb	7,675	6,963
LHV, kJ/kg	17,854	16,198

Table 12. Process mass and energy balance.

INPUTS	**SOT**	**TARGET**
Biomass, tons/day (as received, 26.5% moisture)	1,366	
higher heating value, MMbtu/day	16,451	
tons/day (moisture and ash free)	1,000	
Methanol makeup, tons/day	51.4	44.6
higher heating value, MMbtu/day	1,012	877
Solvent makeup, tons/day	1.10	
higher heating value, MMbtu/day[a]	45	
Hydrogen, lb/day	22,338	29,751
higher heating value, MMbtu/day	1,366	1,819
Natural gas, MMbtu/day HHV[b]	2,368	3,516
Electricity, kW	11,631	12,176
MMbtu/day	953	997
OUTPUTS[b]		
Final bio-oil ("HDO oil"), tons/day	273	354
Barrels per day	1,832	2,374
higher heating value, MMbtu/day	9,385	12,166
ENERGY CONVERSION RATIO (HHV)		
Energy produced/total energy input	0.42	0.51

(a) Assuming a solvent HHV of 40.6 MMbtu/ton, which is similar to that for gasoline.

(b) Natural gas is required for some process heating. Combustible off-gas and char byproducts of the process are burned to supplement natural gas to provide process heat. Off-gas is produced at a rate of 269 MMbtu/day (SOT) and 391 MMbtu/day (TARGET). Char is produced at a rate of 3,522 MMbtu/day (SOT) and 3,485 MMbtu/day (TARGET).

Cost and emissions modeling results using a baseline set of input assumptions are described below. The models are implemented in spreadsheets that facilitate recalculations to explore the impact of alternative assumptions.

Table 13. Annual physical quantities.[a]

	SOT	TARGET
INPUTS		
Biomass, dry tons/yr	273,750	328,500
Methanol, t/yr	14,071	14,643
Solvent, t/yr	301	361
Hydrogen, lb/yr	6,115,053	9,773,196
Electricity, MWh/yr	76,416	95,992
Natural gas, MMbtu/yr	648,174	1,154,851
OUTPUTS		
Bio-oil (HDO oil), bbl/yr	501,416	779,940
Bio-oil (HDO oil), t/yr	74,761	116,289
Bio-oil (HDO oil), million gallons/yr	21.06	32.76
Ash, tons/yr	1,122	1,346

(a) Assuming capacity factor of 75% for SOT and 90% for TARGET.

5.1 Cost model and results

Two equivalent approaches to the financial analysis were developed for estimating the levelized revenue per gallon of bio-oil over the lifetime of the plant that would need to be received to cover all costs, including the desired return on equity. Both approaches allow the user to estimate the levelized cost of producing HDO oil from the plants described by Table 11, Table 12, and Table 13Table , based on estimated total overnight plant capital costs (Table 14) and assumed unit prices for inputs (Table 15). Given the early (scoping-study) stage of project analysis, the overnight capital cost is estimated simplistically as the total bare equipment cost multiplied by a "Lang Factor" to account for all other costs. As noted in Table 14, a factor of 4.5 is applied to the bare equipment cost to estimate the SOT plant overnight capital requirement and 4.0 to estimate the TARGET plant overnight capital. Unit input prices (Table 15) are constant in real terms over the life of the project, or, equivalently, they are levelized values over the assumed 20-year economic plant lifetime.

Approach #1 to financial analysis. The first approach to calculating levelized bio-oil production cost uses the financial parameter assumptions given in Table 16. Interest during construction is added to the overnight cost to estimate the total capital requirement (*TCR*). (Zero salvage value is assumed at the end of the plant's life.) A weighted average cost of capital (*WACC*) is specified and implicitly incorporates debt:equity fraction, cost of debt, return on equity, taxes, property tax, insurance and other factors. The *WACC* is used to calculate annual capital charges:

$$Annual\ Capital\ Charge = TCR\ \cdot CCR$$

where *CCR* is the capital charge rate:

$$CCR = \frac{WACC}{1-(1+WACC)^{-N}}$$

where *N* is the economic lifetime of the project in years. For calculating annual operating costs, the plant is assumed to operate each year of its life from the start with the capacity factors in Table 16.

The resulting annualized costs for the SOT and TARGET plants are given in Table 17. The calculated levelized cost of producing bio-oil is \$3.1/gallon for the SOT plant and \$2.3/gallon for the TARGET plant (expressed in constant 2013\$). It is anticipated that the bio-oil, which contains about 1.5% oxygen, would be co-processed with crude oil at a conventional refinery to produce a fuel that can replace petroleum-derived diesel.[1] A refining margin of \$0.53/gallon is added to the bio-oil production cost to account for this additional processing. This margin is estimated as the 20-year levelized value (2020 to 2039, 7% discount rate) of the difference projected by EIA in the Annual Energy Outlook 2015 Reference Scenario between the US average wholesale \$/gallon price of diesel and the \$/gallon spot price of West Texas Intermediate crude oil.[2] The resulting refinery gate price of the biomass-derived diesel fuel is about 1.3 times the price of petroleum-derived diesel in the SOT case and about equal to the price of petroleum-derived diesel in the TARGET case (Table 17).

Table 14. Estimated capital investment required (2013 $).

	SOT	TARGET
Process equipment (bare)[a]		
Feedstock preparation system	$10,242,045	$10,242,045
1st Stage Liquefaction		
Static Mixer	$15,888	$15,888
High-Pressure Pump 1	$1,000,702	$1,000,702
High-Pressure Pump 2	$1,000,702	$1,000,702
Liquefaction Reactor	$372,368	$372,368
Reactor Heater	$283,770	$283,770
Hot Oil System for Heating	$1,692,517	$1,692,517
Solid Filter[b]	$1,491,871	$678,206
Flash Separator	$494,756	$889,412
Methanol distillation	$1,296,522	$1,807,116
Decanter	$147,089	$144,108
AP Recycle Pump	$82,317	$73,871
AP Treatment Tank	$6,965	$6,379
Solids Conveyor	$41,570	$69,105
2nd Stage Liquefaction		
Static Mixer	$10,776	$0.00
High-Pressure Pump 1	$1,000,699	$0.00
High-Pressure Pump 2	$1,000,699	$0.00
Liquefaction Reactor	$372,368	$0.00
Reactor Heater	$283,770	$0.00
Hot Oil System for Heating	$1,660,374	$0.00
Solid Filter	$458,726	$0.00
Flash Separator	$185,522	$0.00

Table 14 Continue.

HTL Upgrading		
Static Mixer	$12,487	$14,431
High pressure pump 1	$210,202	$250,072
High pressure pump 2	$210,202	$250,072
Reactor Heater	$283,770	$376,904
Hot Oil System for Heating	$806,840	$1,029,064
HDO Reactor	$322,340	$428,133
PSA	$2,733,905	$3,441,263
Feed Product Heat Exchanger	$316,028	$411,324
Product Flash Drum	$84,538	$110,030
Hydrogen Compressor	$1,739,653	$2,264,237
Decanter	$731,279	$951,793
Product Trim Cooler	$365,140	$475,246
Plant Balance		
Solvent Storage Tank	$149,600	$149,600
Cooling Water Pump	$132,112	$171,950
HTL Storage	$217,204	$282,701
Wastewater Storage	$101,533	$101,533
WWT anaerobic/aerobic digestion	$596,951	$596,951
Plant Air Compressor	$25,791	$25,791
Hot Oil	$1,156,405	$1,156,405
Total bare equipment cost	**$34,671,515**	**$31,994,235**
Total overnight capital cost[c]	**$156,021,816**	**$127,976,942**

(a) Provided by Southern Research[1].

(b) The solid filter reduced in the target case as solid generation is significantly minimized due to enhancement of light oil yield.

(c) Estimated by multiplying bare equipment cost by a "Lang Factor" of 4.5 for SOT and 4.0 for TARGET. A Lang Factor between 4 and 5 is typical one to use for an initial capital cost estimate for a project that uses well-established ("Nth plant") technologies in the petrochemical industry. For a first-of-a-kind plant, a higher Lang Factor (6 or 7) would be more appropriate.

Table 15. Assumed unit prices (baseline) for SOT and TARGET.[a]

Biomass, $/dry ton ($/ton AR)	50[b] (37)
Methanol, $/ton	550[c]
Solvent, $/MMbtu	16[d]
Hydrogen, $/lb	1.0[e]
Electricity, $/MWh	70[f]
Natural gas , $/MMbtu	6.9[g]
Catalysts and chemicals, $/ton of HDO oil	36.1[h]
Ash disposal, $/ton	18[h]
RIN value, $ per gallon	0[i]

(a) These represent levelized prices over an assumed 20-year economic plant operating lifetime.

(b) SR intends to use biomass feedstock in particle size of 300-500 microns in the commercial process. For comparison, typical delivered woody-biomass costs in the South-Central US in 2014 included $33/dry ton for unprocessed forest residues, $58/dt for mill-residue chips, and $76/dt for pulpwood chips.[6] Capital and operation cost of making fine wood particles has been included in the cost analysis.

(c) The Methanex North America monthly average non-discounted methanol reference price in 2014 was $541 per metric ton.[7]

(d) Assuming solvent has properties similar to gasoline, this is approximately $2/gallon of gasoline equivalent.

(e) Estimated hydrogen production cost based on[8] (excluding compression, storage, and dispensing), assuming current steam methane reforming technology and natural gas prices projected for industrial customers in the DOE Annual Energy Outlook 2012 Reference scenario.

(f) For comparison, the US average price for industrial users in 2012 was $67/MWh and ranged from $41/MWh in Washington state to $127/MWh in Connecticut.[9]

(g) This is a 20-year levelized price (2020 to 2039, 7% discount rate) to U.S. industrial users projected in the *Annual Energy Outlook 2015* Reference Scenario.[2]

(h) Provided by SouthernResearch.[1]

(i) Baseline cost results here assume zero RIN credits. For reference RIN values in mid-March 2015 were about $0.65/gallon for ethanol and $0.75 for advanced biofuels.[10]

Table 16. Financial assumptions for simplified levelized cost calculation.

	SOT	TARGET
Interest during construction (% of overnight capital)	7.3%	
Total capital investment required (million 2013$)[a]	$167	$137
Weighted average cost of capital (real discount rate)	8.2%/year[b]	
Economic lifetime	20 years	
Annual capital charge rate	10.3%/year	
Annual capacity factor	75%	90%

(a) Sum of overnight capital and interest during construction.

(b) This corresponds to a 60:40 debt:equity ratio, a 5% (real) loan interest rate, and a 13% (real) rate of return on equity, without consideration of taxes.

Table 17. Levelized production costs (using financial assumptions in Table 21).

	$/year		$/gallon HDO oil	
	SOT	TARGET	SOT	TARGET
Capital charges	17.3	14.2	0.82	0.43
Operation and maintenance[a]	7.8	6.4	0.37	0.20
Biomass feedstock	13.7	16.4	0.65	0.50
Methanol makeup	7.6	7.9	0.36	0.24
Solvent makeup	0.20	0.23	0.01	0.01
Hydrogen	6.1	9.8	0.29	0.30
Electricity	5.4	6.7	0.25	0.21
Natural gas	4.5	8.0	0.21	0.24
Catalysts and chemicals	2.7	4.2	0.13	0.13
Ash disposal	0.02	0.02	0.00	0.00
Levelized Production Cost	**64.0**	**72.6**	**3.10**	**2.25**
Refining margin			**0.53**	**0.53**
Sale price for finished (diesel-like) fuel, $/gal			**3.6**	**2.8**
Price relative to 2014 petroleum-derived diesel[b]			**1.3**	**1.0**

(a) Annual operating and maintenance costs are estimated as 5% of the overnight capital cost values given in Table 19.

(b) This is the ratio of finished (diesel-like) fuel price to average US petroleum-derived diesel price to resellers in 2014,[11] when the average refiner acquisition cost for crude oil was $92/barrel.

Approach #2 to financial analysis. The second approach is a year-by-year discounted cash flow (DCF) analysis following the methodology typically used in design reports from the National Renewable Energy Laboratory.[3] The DCF calculation includes considerably more detail than Approach #1, but gives essentially the same result for levelized cost per gallon of bio-oil when the input assumptions are self-consistent between the two approaches.

The DCF approach requires a greater number of assumptions than Approach #1, including specifying the real rate of return on equity (13% assumed for baseline), real loan interest rate (5%) and term (10 years), equity fraction of capital invested (40%), project lifetime (20 years), the combined federal and state tax rate (40%), and depreciation schedule (the US modified accelerated cost recovery schedule – MACRS – is assumed.) Additionally, a plant construction time of 3 years is assumed, with 8% of the total overnight capital spent in the first year, 60% in the second, and 32% in the final construction year. Working capital is included in the DCF model, and this is assumed to be 5% of the overnight capital cost. A plant startup period of 6 months is assumed, during which only 50% of full-load revenues are received and 50% of variable costs are expended. During the half-year start-up period, O&M costs are assumed to be 75% of the full-load level. Beyond the startup period, the plant operates with the capacity factors given in Table 16.

Once all of the above input assumptions have been entered, the model does year-by-year cash-flow calculations beginning with the first year of construction (year -3). Bio-oil revenues start to arrive and loan repayments begin with year 1, along with payment for other costs (O&M, biomass, other variable costs, depreciation, etc.). The annual bio-oil revenue is the product of the number of gallons produced and an assumed levelized bio-oil selling price per gallon. The model calculates the bio-oil selling price that produces a zero net present value for the project as a whole. This "minimum fuel selling price" (MFSP) is the price that will allow all plant costs to be covered, including return on equity and interest on debt. With the assumptions noted in the prior paragraph, the MFSP is $3.4/gallon for the SOT plant and $2.4/gallon for the TARGET plant.

5.2 Fuel-cycle greenhouse gas emissions model and results

Fuel-cycle greenhouse gas emissions associated with the bio-oil product are estimated taking into account emissions from the liquefaction facility itself, as well as emissions associated with production and delivery of the biomass feedstock, with production and delivery of other process inputs, with transport and refining of the bio-oil, and finally with combustion of the fuel product (Fig. 12).

Because many processes must be considered in estimating the fuel-cycle emissions and several assumptions must be made about each process to quantify its emissions, for the GHG analysis we have relied to the extent feasible on process GHG analyses done by engineers at the National Energy Technology Laboratory. Emissions for an extensive set of processes have been analyzed in considerable detail within a self-consistent framework by NETL engineers.[4] Where NETL sources were not available for particular elements of the GHG emissions modeling, other well-respected sources were consulted, as documented in the notes of Table 18, which shows GHG emission results for the SOT and TARGET plants. The table results are organized into the five areas shown Fig. 12.

Biomass production and delivery contributes net negative emissions to the fuel-cycle as a result of photosynthetic absorption of CO_2 from the atmosphere. The largest positive emission in the biomass supply area is attributed to indirect land use change (ILUC). Given the large uncertainties in quantifying ILUC impacts,[5] overall results are given in Table 18 (at the bottom) with and with ILUC included.

Production of liquefaction process inputs assumes that fossil fuels are used to make the inputs. The production of hydrogen via steam methane reforming and of electricity via natural gas combined cycle are the two largest emission sources in this process area.

Liquefaction process emissions assume that solid and gaseous byproducts are combusted, supplemented by natural gas combustion, to provide requisite heat for the process (Table 19). Liquid effluents of the process carry considerable carbon content that is assumed to be released to the atmosphere when the liquids are treated before release to the environment. Liquid effluent emissions are reduced considerably from the SOT to the TARGET plant because process modification enable more of the carbon that goes into the liquids in the SOT design to be converted into HDO oil. However, the fuel-cycle GHG emissions analysis counts emissions from both liquid effluents and from HDO oil combustion. This mutes the impact on the total fuel-cycle carbon footprint of shifting carbon from liquid effluents to HDO oil.

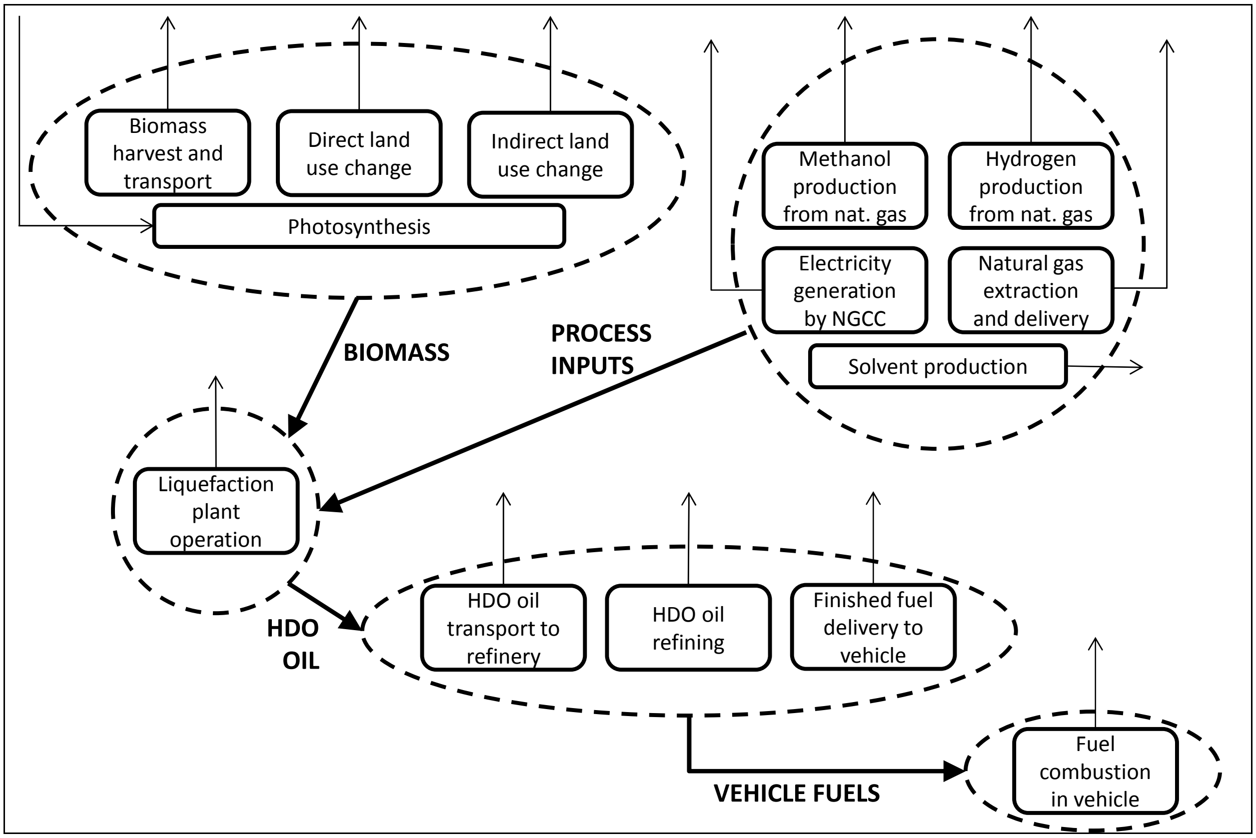

Figure 12. Representation of system greenhouse gas flows. The thin-line arrows represent GHG flows to or from the atmosphere. Each of these emissions is included in the fuel-cycle GHG estimates.

HDO oil transportation and refining assume that the final product from the liquefaction facility is delivered to a refinery for final processing into vehicle fuels. Emissions are modeled based on those for transportation and refining of crude oil.

Fuel combustion in vehicles is assumed to release all carbon bound in the HDO oil to the atmosphere.

Table 18. Fuel-cycle greenhouse gas emission balances.

	metric tCO2e/day		kgCO2e/MMBTU$_{LHV}$ HDO oil	
	SOT	**TARGET**	**SOT**	**TARGET**
Biomass Production & Delivery	**- 1,725**	**- 1,725**	**- 183.8**	**- 141.8**
Photosynthesis[a]	- 1954	- 1954	- 208.2	- 160.6
Harvest & transport[b]	69	69	7.3	5.6
Direct land use change[b]	34	34	3.6	2.8
Indirect land use change[b]	126	126	13.5	10.4
Production of Liquefaction Process Inputs	**336**	**403**	**35.8**	**33.1**
Hydrogen supply emissions[c]	147	196	15.7	16.1
Electricity generation/supply[d]	136	143	14.5	11.7
Natural gas extraction and delivery[e]	30	44	3.1	3.6
Makeup MeOH (production of)[f]	22	19	2.4	1.6
Makeup solvent (production of)[g]	1	1	0.1	0.1
Liquefaction Process Emissions[h]	**1,228**	**1,038**	**130.8**	**85.3**
Solids (Char+coke) combustion	398	422	42.4	34.6
Liquid plant effluents	649	372	69.2	30.6
Off-gas combustion	55	57	5.8	4.7
Natural gas combustion	126	187	13.4	15.4
HDO Oil Transport and Refining	**116**	**151**	**12.4**	**12.4**
Bio-oil transport to refinery[i]	15	19	1.6	1.6
Refinery emissions[j]	92	120	9.8	9.8
Finished fuel transport to user[k]	9	12	1.0	1.0
Fuel combustion in vehicle[l]	**852**	**1,105**	**90.8**	**90.8**
TOTAL NET GHG EMISSIONS	**807**	**970**	**86.0**	**79.7**
Total, % of equivalent petroleum-fuel emissions[m]			**90%**	**83%**
RESULTS IF INDIRECT LAND USE CHANGE IS ASSUMED TO BE ZERO				
Total net GHG emissions	**681**	**844**	**72.6**	**69.4**
Total, % of equivalent petroleum-fuel emissions			**76%**	**73%**

(a) The amount of carbon uptake by photosynthesis is assumed to be the amount of carbon in the biomass input to the liquefaction plant.

(b) Includes emissions of CO_2, CH_4, N_2O, and SF_6, for southern pine plantation biomass, as reported by Cooney[12] based on Skone, *et al*[13] and using the following 100-year global warming potentials to convert to CO_{2e}: 25 for CH_4, 298 for N_2O, and 22,800 for SF_6. Emissions (kgCO2e/metric tonne as-received biomass) are 45.2 for stand management, harvest and transport; 22.3 for direct land use change; and 83.3 for indirect land use change.

(c) Hydrogen is assumed to be produced by steam methane reforming of natural gas, for which the lifecycle GHG emissions are 14.56 kgCO_{2e} per kg of hydrogen.[14]

(d) Electricity is assumed to be supplied from a natural gas combined cycle characterized by having lifecycle GHG emissions of 488 kgCO2e/MWh.[15]
(e) GHG emissions for production and delivery of natural gas to the liquefaction plant is assumed to be 12.4 kgCO2e per million BTU_{HHV} of gas delivered, based on [15].
(f) Makeup methanol is assumed to be produced from natural gas, with associated GHG emissions ("well-to-tank," i.e., excluding combustion) of 25 $kgCO_{2e}$ per million BTU_{LHV}, or 432 kgCO2e per short ton.[16]
(g) The production of makeup solvent is assumed to generate the same GHG emissions, "well-to-tank," as the production of gasoline: 838 $kgCO_{2e}$ per short ton, based on.
(h) Except for natural gas combustion, the figures in this section are based on the carbon content of process flows provided by Southern Research[1]. Natural gas combustion is assumed to release 53.2 $kgCO_2/MMBTU_{HHV}$.
(i) Emissions are assumed to be the same as for crude oil transport to a refinery: 7.99 $kgCO_{2e}$/barrel delivered, based on [17].
(j) Emissions are assumed to be the same as for refining of crude oil: 50.4 $kgCO_{2e}$/barrel crude entering a refinery, based on [17].
(k) Emissions are assumed to be the same as transport of finished fuels from a petroleum refinery: 5.0 $kgCO_{2e}$/barrel crude entering the refinery, based on [17].
(l) Based on carbon content of HDO oil product [1].
(m) This is the ratio of calculated fuel-cycle emissions for the bio-oil fuels to the average fuel-cycle emissions for petroleum-derived transportation fuels in the U.S. in 2005. The latter is estimated to be 95.6 $kgCO2e/MMBTU_{LHV}$. [17]

As detailed in Table 18, the total fuel-cycle GHG emissions for fuels produced by the SOT liquefaction process design are estimated to be from 10% to 24% below emissions for equivalent petroleum-derived fuels (depending on whether or not ILUC impacts are included in the estimate). Emissions are only moderately lower for the TARGET plant design (17% to 27% below petroleum-derived fuel emissions) than for the SOT plant because the higher yield of HDO oil in the TARGET design is only achieved with greater consumption of fossil-fuel derived hydrogen and natural gas.

Table 19. Carbon balance for the conversion facility.

	kgC/day	
	SOT	TARGET
CARBON IN	**588**	**602**
Biomass	533	533
Natural gas	34	51
Methanol makeup	19	17
Solvent makeup	1	1
CARBON OUT	**586**	**601**
HDO oil	232	301
Aqueous phase	177	101
Combustion flue gases	177	199

6. Refinery Collaboration

The objective of refinery collaboration is to establish at least one refinery partner willing to evaluate the liquefaction bio-oil samples for co-processing with petroleum feed in refinery process and willing to work collaboratively to scale up the technology if the evaluation shows promise.

Potential refinery partners were evaluated for suitability based on their financial strength and preliminary discussions were carried out with a number of refinery companies. Five refinery companies were contacted but they were reluctant to collaborate for various reasons. These reasons include already ongoing project in the area or unwillingness to start a new initiative in biofuels. SR made other attempts to develop a refinery partnership through various outreach activities, including a News Release and advertisement of the project at biofuels conferences such as Advanced Biofuels Leadership Conference.

Attempts have continued to develop a partnership with three selected refinery companies. Onsite meetings have been held two of them. The overall process design and results have been presented in these meetings. Other outreach activities have included presentations at the tcBiomass 2013 conference, annual AIChE meeting 2013 and Lignocellulosics conference 2014. Additional presentations are planned in November at the tcBiomass 2015 and annual AIChE meeting 2015.

A leading catalyst company participated in developing Southern Research's bio-oil upgrading process and provided support in contacting refinery companies. It provided Southern with three hydrotreating catalysts and also guided Southern Research's team on the hydrotreating conditions with their proprietary process. Detailed bio-oil hydrotreating results were discussed with senior Engineers and Directors at the catalyst company and they are summarized in Section 5.

Through the discussions with refinery industry, several major hurdles that prevent bio-oil from being accepted in conventional refinery process have been identified. These include:

1. Refinery companies are not willing to accept bio-oil with more than 5-10% oxygen content for blending at 20 %. The exothermic HDO reaction is difficult to control in a large-scale refinery process. (Ideal co-processing feed should have oxygen content no more than 1%)
2. Incomplete compositional analysis of bio-oil cannot help refinery experts to identify whether bio-oil generated from SR's liquefaction process is a potential feed for co-processing with petroleum feeds
3. Bio-oil needs to be stabilized for less coke formation and clogging during co-processing.
4. Bio-oil is better miscible with petroleum feeds, so it can be blended with petroleum distillates and dilute the oxygen content of bio-oil to <1% for co-processing
5. Bio-oil physicochemical properties need to be as closer to that of petroleum oil as possible.

The attempts to collaborate with Refinery Company on co-processing liquefaction bio-oil with petroleum feed have been continued through the whole period of this project. However, due to a sudden crash of crude-oil market (from ~$100/barrel to ~$45/barrel), the petroleum companies, have even less interest in investing on biofuel related projects, particularly on bio-oil. The cheap crude oil price becomes another major hurdle preventing Southern Research from collaborating with refinery companies.

7. Project Management and Reporting

All project quarterly reports have been submitted to DOE project manager on time. Project progress meeting and briefing have been held at DOE and Southern Research office. The project results have been peer-reviewed in 2013 and 2015. Project results were summarized and submitted to DOE Data Mining group at NREL for technology assessment t. A final project report has been prepared for submission.

Publications, Conference Papers and Patent Application

Santosh Gangwal and Kevin McCabe, Mild Biomass Liquefaction Process for Economic Production of Stabilized Refinery-Ready Bio-oils, 2013 TC Biomass Conference, Chicago, IL, September 3-6, 2013.

Santosh Gangwal, Kevin McCabe and Kelly Mastro, Development of a Biomass Liquefaction Process for Stabilized Refinery-Ready Bio-oils, 2013 AIChE Annual Conference, San Francisco, CA, November 3-8, 2013.

Jiajia (August) Meng, Kevin McCabe, Kelly Mastro and Santosh Gangwal, Mild Biomass Liquefaction Process for Economic Production of Stabilized Refinery-Ready Bio-oils, 11th World Congress on Industrial Biotechnology, Philadelphia, PA, May 12-15, 2014.

Jiajia (August) Meng, Kevin McCabe, Kelly Mastro and Santosh Gangwal, Renewable Fuel Production via Mild Biomass Liquefaction: Process Integration, TEA and LCA, Bio Pacific Rim Summit on Industrial Biotechnology & Bioenergy, San Diego, CA, December 7-9, 2014.

Kelly Mastro, Jiajia (August) Meng, Kevin McCabe, and Santosh Gangwal, Renewable Fuel Production via Mild Biomass Liquefaction Process, 250th ACS National Meeting and Exposition, Boston, MA, August 16-20, 2015.

Jiajia (August) Meng, Kevin McCabe, Kelly Mastro, Eric Larson and Santosh Gangwal, Renewable Fuel Production via Methanol-Assisted Biomass Liquefaction Process, 2015 AIChE Annual Conference, Salt Lake City, UT, November 8-13, 2015.

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