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OPPORTUNITIES FOR BIORENEWABLES IN OIL REFINERIES

FINAL TECHNICAL REPORT

SUBMITTED TO: U.S. DEPARTMENT OF ENERGY



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I EXECUTIVE SUMMARY

The purpose of this study was to evaluate the potential for using biorenewable feedstocks in oil refineries. Economic analyses were conducted, with support from process modeling and proof of principle experiments, to assess a variety of potential processes and configurations. The study identified a number of promising opportunities for biorenewables in existing or new refining operations.

The work was performed as a joint project with the National Renewable Energy Laboratory (NREL), and Pacific Northwest National Laboratory (PNNL). NREL provided pyrolysis oil feedstocks and biorenewable expertise. PNNL provided feedstocks and biorenewable processing expertise; PNNL also conducted some of the proof of principle experiments. The DOE provided $80,000 of the total $230,000 funding for the project.

The study considered two primary alternatives: the production of biodiesel and green diesel from vegetable oils and greases and opportunities for utilization of pyrolysis oil. Green diesel produced from hydrotreating vegetable oil and grease was identified as one of the best options for refiners, agricultural producers, and forest products producers. Green diesel has superior product properties, requires less capital investment to produce, and has a lower environmental impact than biodiesel. Green diesel is economically attractive under two conditions: (1) using a low-cost feedstock such as brown grease; or (2) if vegetable oil feedstocks are subsidized.. Green gasoline and green olefins, which are produced by cracking vegetable oils and grease in an FCC unit, are also economically attractive, particularly if eligible for subsidies.

Processing of pyrolysis oils represents a longer term opportunity, since pyrolysis oils are currently available only in small quantities. However, unlike vegetable oils and greases, they have the potential to provide a significant portion of future transportation fuels (60%). The study evaluated options for using crude pyrolysis oil as well as two of its fractions – pyrolytic lignin and the water-soluble phase .

Experimental work confirmed that pyrolytic lignin can be converted to gasoline with reasonable H_2 consumption using mild hydrotreating followed by hydrocracking. The economics of this process are increasingly attractive with increased crude oil price or decreased pyrolysis oil price with increased production. At a price of $50/bbl for crude, the analysis predicted payback in three years.

The water-soluble phase of pyrolysis oil is suitable for generating hydrogen. Most, or all, of the hydrogen used in a typical refinery can be provided by steam reforming 5200 bpd of the water soluble portion of pyrolysis oil. A small portion of this hydrogen can be used to provide hydrogen for hydrotreating the pyrolytic lignin to make gasoline. The economics of hydrogen formation from the water soluble portion of pyrolysis oil become attractive when there is a CO_2 credit of $30/ton and pyrolysis oil cost is $10/bbl. Since the pyrolysis oil used for hydrogen production would replace purchased natural gas, this is a way to reduce nearly 20% of refinery emissions of climate-active CO_2. However, pyrolysis oil price must drop before this process becomes economically attractive.

Crude pyrolysis oil can be substituted for purchased natural gas as a fuel in refinery boilers and furnaces, also reducing CO_2 emissions. Pyrolysis oil is less costly than natural gas by $1.2/MMBTU and therefore represents an economically viable substitute for natural gas in a refinery setting.

The high oxygen content of pyrolysis oil imposes constraints on processing in standard metallurgy and current economics for hydrotreating pyrolysis oil assume a standalone unit is required. Initial hydrothermal treatment under mild conditions may provide a low cost approach

to reduce the oxygen content and allow processed in standard equipment. More experimental work is needed to determine the viability and economic impact of hydrothermal treatment.

Hydrotreating and hydrocracking, technologies which were developed for oil refineries, were found to be particularly useful for processing vegetable oil, greases, and pyrolysis oils. The level of hydrogen required for hydrotreating can be controlled by processing conditions and catalyst, since the same materials which catalyze hydrodeoxygenation also catalyze decarboxylation. Optimization of this technology for biorefineries will lead to better utilization of these biofeedstocks for conversion to fuels and chemicals.

A key barrier to the use of biorenewables in oil refineries is that available quantities are small relative to the size of most refinery processing equipment. Refiners are naturally resistant to risking catalysts and run time in large petroleum processing units, for the sake of processing small amounts of biofeedstocks. Skid mounted, standalone green diesel, or pyrolysis oil hydrotreating units solve this problem by allowing biorenewables to be processed separately from petroleum fractions. These skid mounted units could also be used by agricultural and forest producers.

II STUDY GOALS AND BASIS

II.1 STUDY GOALS

The overall goal of this study was to evaluate the economics of using biomass-derived feedstocks (biofeedstocks) in petroleum refineries. The technical work was divided into three tasks: modeling of refinery options to project yields and costs (Task 1); a variety of scoping experiments (Task 2); and, analysis of costs and process economics (Task 3).

Several alternatives were evaluated:

- Processing of biofeedstocks in existing refinery equipment
- Coprocessing of biofeedstocks with crude oil fractions in existing refinery equipment
- Blending biofeedstocks with petroleum feeds

In addition, new processing steps were evaluated that would enable more effective use of biofeedstocks in refining operations.

Two classes of biofeedstocks were considered:

- Vegetable oils and greases derived from crops such as corn, soy, canola and rapeseed
- Pyrolysis oil derived from forest waste

A number of processing options was considered for each type of biofeedstock. In each case, one or more candidate processing schemes was modeled. Experiments were conducted as needed to determine the key processing parameters required to understand cost and economic impact of biofeedstock use in a particular process. Cost estimates were developed and used in a broader evaluation of the potential process economics. This report summarizes the results of the process models and supporting experiments. Additional details are provided in the supporting Appendix.

This Final Report is organized by processing option, rather than by task, to more clearly present the alternatives. The basis and assumptions used in the study are outlined in Section II.2. Section III describes opportunities for utilizing vegetable oils and greases, particularly in the production of biofuels. Section IV describes the evaluation of opportunities for processing or coprocessing pyrolysis oil to produce gasoline, aromatics or hydrogen. The value of processing Fischer-Tropsch liquids in biorefineries was also evaluated, described in Section V. Lists of acronyms and abbreviations and key references are located in Sections VI and VII, respectively. The Appendix provides a summary of key experiments (Appendix Tables 1 and 2) and additional background for the study basis.

II.2 STUDY BASIS

II.2.1 Market and Supplies

Table 1. Availability of biorenewable feedstocks in U.S.[1,2,3,4,5]

	Definition	U.S. Production (bpd)	Available for Conversion to Fuels (bpd)
Vegetable oils	Produced from soybeans, corn, canola, palm	194,000	33,500
Recycled products	Yellow grease, brown (trap) grease	51,700	33,800
Animal fats	Tallow, lard, fish oil	71,000	32,500
Pyrolysis oil	Produced by pyrolysis of wood slash, waste and other biomass waste	1,500	750

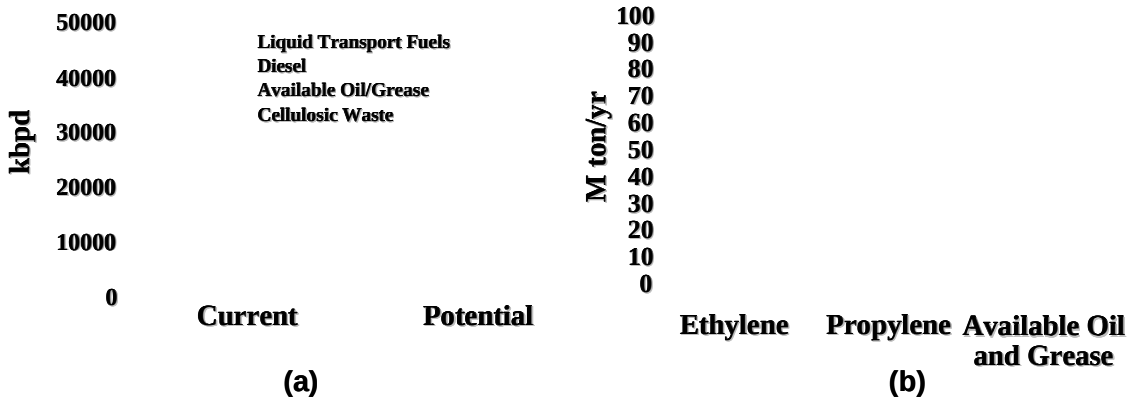


Figure 1. Global feedstock supplies.
(a) Availability of oil and grease relative to other fuels.[6,7 8,9]
(b) Potential contribution to chemicals production.[10,11]

Roughly 100,000 bpd of oil and grease are currently available in the U.S. for conversion to fuels (Table 1).Oils and grease are available today and are likely to make an increasing contribution to the world's fuel supply in the near term, in part due to government-mandated targets (see Appendix, Table 3). For example, the U.S. has mandated that 2.5% of diesel be generated from biorenewable sources by 2010. However, quantities of oil and grease are limited. In contrast, very little pyrolysis oil is produced at present but the potential supply is much larger. As shown in Figure 1 (a), significant levels of cellulosic waste are available globally for production of pyrolysis oil if conversion to transportation fuels becomes economically attractive. Therefore, pyrolysis oils have a far greater long term potential for replacing transportation fuels. Chemicals are a much smaller market than transportation fuels and oils and grease feedstocks could play a significant role, particularly for olefin production, as shown in Figure 1.

II.2.2 Feedstock costs and product prices

The study took into account both feedstock costs and the projected prices of potential products. The economic analysis was primarily based on a West Texas Intermediate (WTI) crude feedstock price of $40 per barrel. The impacts of price increases to $50 and $60 per barrel of crude were also explored. Biofeedstock prices were based upon an average of the 2003 – 2004 values reported in the Chemical Marketing reporter (See Appendix, Table 4). Figure 2 shows the trend in feedstock prices in $/ton during the 2003 – 2004 period.

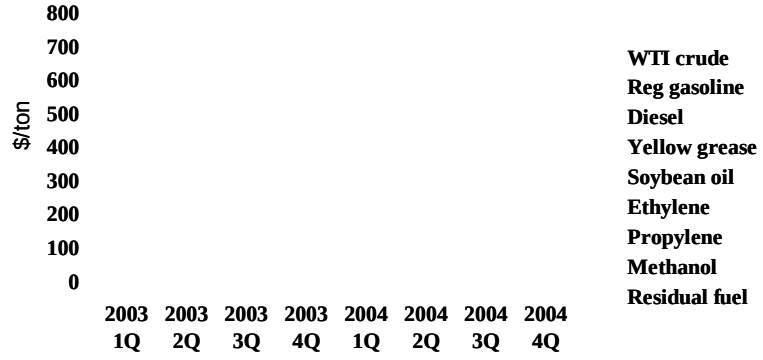


Figure 2- Average feedstock prices.
Note that $306/ton = $40/bbl for WTI crude (2nd quarter 2004)

A number of factors impact the estimated price of biofuels. The following factors were included in the analysis:

- **Capital costs.** Capital costs were estimated for equipment modifications or for new plants, depending upon process requirements.
- **Transportation costs.** Transportation costs vary depending on the location of the refinery and the location of the biofeedstock. A number of U.S. refineries are located near sources of biomass feedstock, specifically oil and grease production facilities and agricultural and wood resources (Appendix, Figures 1 and 2). A transportation charge of $2 per barrel was assumed for biofeedstocks based on typical rail transportation costs for grease and oils.
- **CO_2 credits.** The use of pyrolysis oil as a fuel would generate a CO_2 credit which could be traded. Currently CO_2 is trading for $10/ton but is expected to reach $30/ton in 5 years.
- **Subsidies**. Potential subsidies were calculated based on the subsidies for biodiesel shown in Table 5 of the Appendix.
- **Cetane and octane numbers.** Cetane number (see Section III.3) affects the price of both green diesel and biodiesel. The value of $0.13/cetane-bbl was used to reflect the impact of cetane number on prices; the impact of octane number was represented as $0.50/octane-bbl.

Figure 3 compares the prices of biofeedstocks projected in this study to those of petroleum-based feedstocks. While some biofeedstocks are significantly more expensive than petroleum-based alternatives, others are expected to be less expensive, particularly if supported with government subsidies.

The assumptions used to project the cost of pyrolysis oil are summarized in Table 6 and Table 7 of the Appendix. In the best case, the projected cost of $4.8/MMBTU for pyrolysis oil is significantly higher than that of fuel oil ($4.2/MMBTU) on a heating value basis. Subtracting a $30/ton petroleum feedstock price credit would reduce the pyrolysis oil cost to $4.1/MMBTU, but inclusion of transportation charges increases the cost of pyrolysis oil to $4.7/MMBTU, still significantly higher than heavy fuel oil. A major factor is a capital charge of $81MM for a 6800 bpd pyrolysis unit, which boosts pyrolysis oil from $9/bbl to $16/bbl in the case of a $30/ton feedstock.

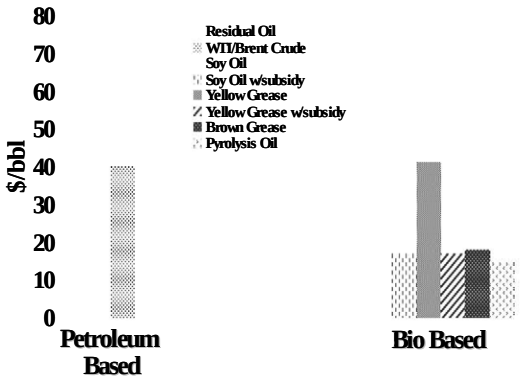


Figure 3. Biorenewable and petroleum feedstock prices.

II.2.3 Refinery Basis

The study was based upon a standard 150,000 bpd U.S. oil refinery. Two typical configurations and process units are pictured in Figure 4 and Figure 5. Almost all refineries contain fluid catalytic crackers (FCC's), reformers and a variety of hydrotreaters. Many refineries contain hydrocrackers which crack vacuum gas oil (VGO) to make gasoline or diesel.

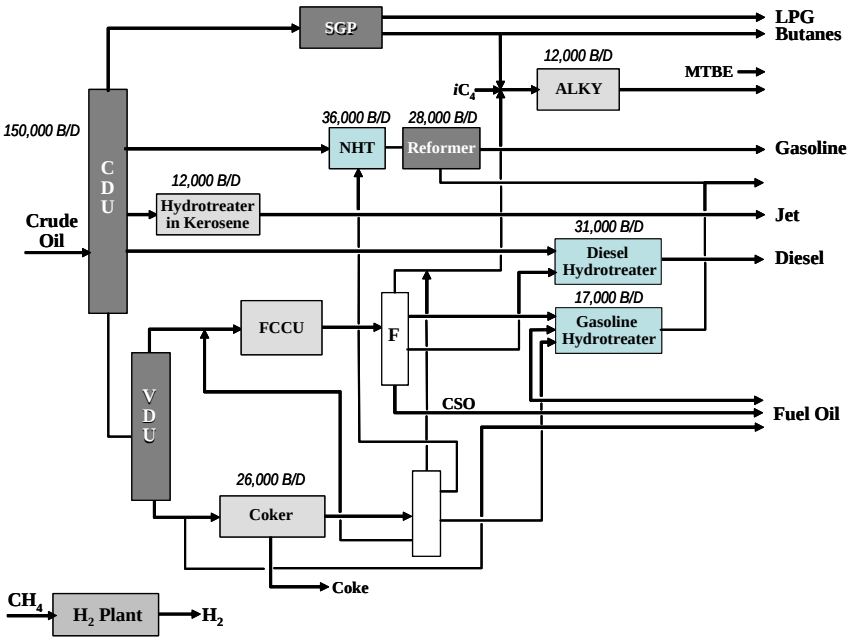


Figure 4. Typical U.S. refinery.

The ability to process biofeedstocks in existing refineries is affected by their high oxygen and acid content. For example, oils and greases typically contain 11-12% oxygen while pyrolysis oils may contain 35-45% oxygen. The acidity of feeds processed in a crude oil refinery is typically measured by the Total Acid Neutralization (TAN) number, defined as the milligrams of potassium hydroxide required to neutralize one gram stock. The TAN numbers for grease and pyrolysis oil make it difficult to process these materials in standard refinery equipment. However they may be processed in 317 stainless steel clad vessels. Other properties of typical biofeedstocks are summarized in Table 8 of the Appendix.

Some of the biofeedstock processing options considered in the study require added hydrogen. Almost all refineries include hydrogen plants to supply hydrogen for hydrotreatment to remove sulfur from diesel and gasoline. The economic analyses presented here assumed an average U.S. hydrogen plant supplying 25 million cubic feet per day of hydrogen using a natural gas feed.

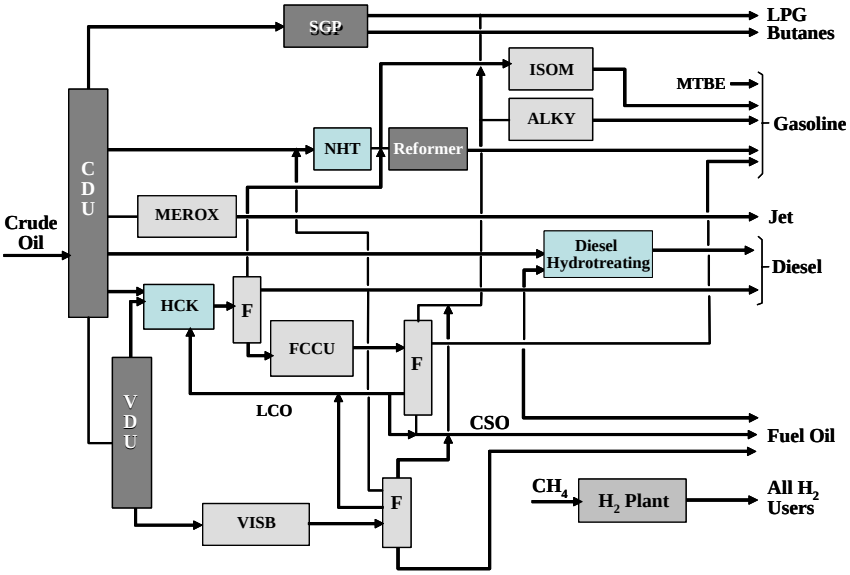


Figure 5. Typical U.S. hydrocracking refinery.

III REFINERY OPPORTUNITIES FOR VEGETABLE OILS AND GREASE

Five separate processing routes for vegetable oil and grease were compared, including biodiesel, green diesel, green gasoline, green olefins and green detergent. The alternatives are illustrated in Figure 6. Biodiesel is differentiated from green diesel in the study. Biodiesel is typically composed of fatty acid methyl esters (FAME). "Green diesel" refers to an acceptable diesel pool blend component produced from a suitable biomass. Green diesel here refers to hydrocarbons produced from biofeedstocks that boil in a typical distillate fuel boiling range and do not contain oxygen in their molecular structure.

Biodiesel production is discussed in Section III.1, together with enabling technologies to facilitate the use of existing refining facilities. Green diesel production by either coprocessing in existing units or processing in new standalone units is evaluated in Section III.2. Biodiesel and green diesel are compared in Section III.3. The production of green gasoline and olefins is reviewed in Section III.4. This section concludes with an overall assessment of process economics and life cycle analysis in Section III.5.

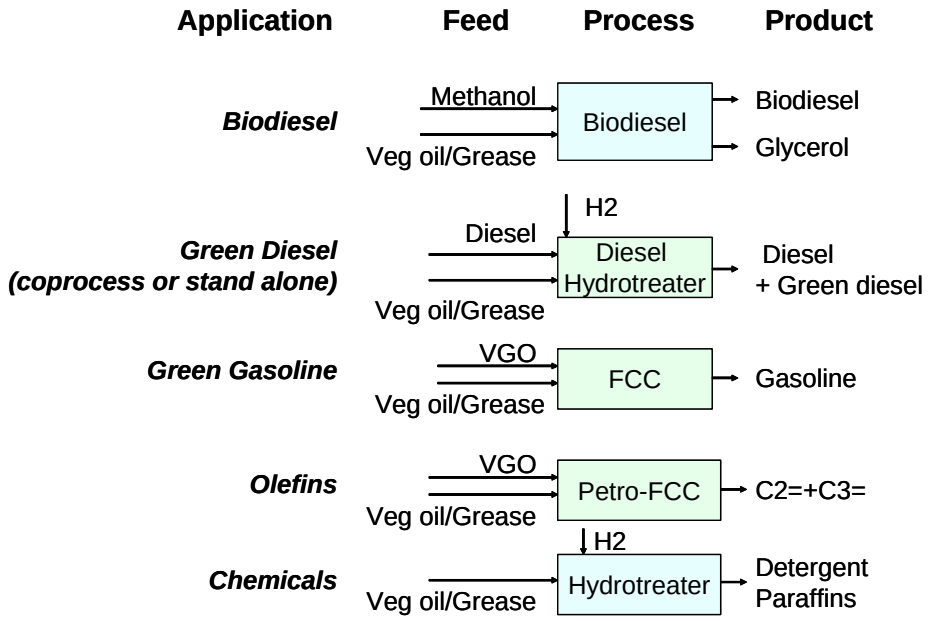


Figure 6. Vegetable oil and grease processing routes.

III.1 BIODIESEL (FATTY ACID METHYL ESTER) PRODUCTION

Due to environmental regulations and changing requirements in fuel specifications, the processing requirements for petroleum products are changing. For example, limits placed on the amount of sulfur in motor fuels have led certain refiners to install new hydrotreating capacity while in some cases shutting down existing treating units. Such events can provide the refiner an opportunity to retrofit existing process equipment, such as storage tanks, pumps, heat exchangers, reactors, separators, and columns, to bio-fuel production. The economic viability of such retrofits is highly dependent on availability and cost of renewable feedstock(s) and the markets for the refined products. The study investigated options and enablers for retrofitting existing units to produce fatty acid methyl esters (FAME).

III.1.1 Fatty Acid Methyl Ester Production in Existing Refining Units

The study considered two specific examples of retrofitting existing refining equipment to Fatty Acid Methyl Ester (FAME) production from biofeedstocks:

- retrofitting a UOP Merox unit, and
- retrofitting a UOP MTBE unit.

In both cases, there is potential to significantly reduce the investment cost associated with FAME production, not only within the battery limits of the unit but also by using existing refinery infrastructure to minimize the overall costs.

Merox Unit Retrofit

UOP Merox (mercaptan oxidation) units have been used by refiners for over 50 years to remove mercaptan compounds from light fuel streams and to sweeten gasoline and jet fuel streams. In the Merox process, mercaptans are catalytically converted to non-odorous disulfide compounds. Depending on the application, one of several different processing schemes may be employed, involving mercaptan extraction or fixed-bed sweetening. Four alternatives are illustrated in Figure 7.

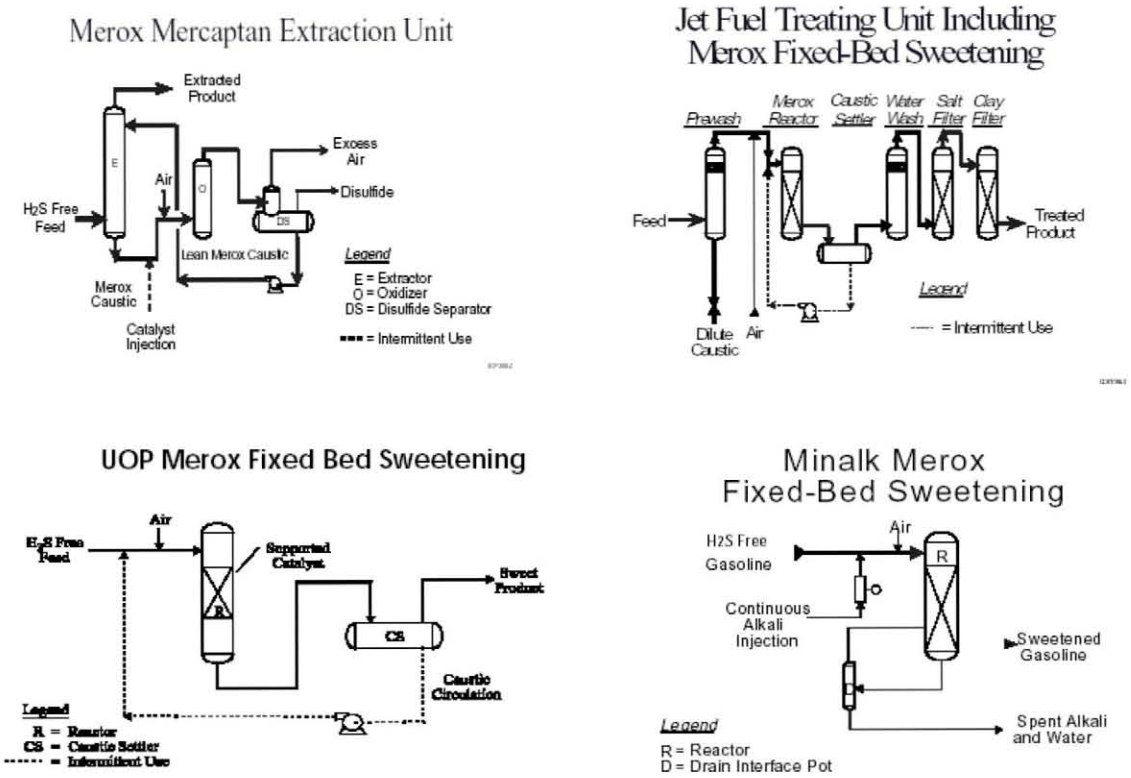


Figure 7. UOP Merox processing schemes.

When a new hydrotreater is installed to lower the amount of sulfur in a gasoline product, existing Merox equipment can become available for retrofit to bio-fuel service. For example, existing liquid extraction columns can be used as a feed or product wash column in a FAME production plant. Likewise, existing pumps, exchangers, reactors, separators, and caustic handling equipment can be reused in the esterification of soybean or rapeseed oil.

Figure 8 illustrates a potential retrofit application wherein existing extraction and fixed bed conversion equipment is reused. The retrofit requires that a heterogeneous catalyst be developed for use in conjunction with an existing Merox fixed-bed reactor/separator to trans-esterify triglycerides in the presence of excess methanol and phase separate the crude glycerol product. Either a mixing device and/or co-solvent might be used to ensure adequate mixing of the triglyceride and methanol in the reactor,

The FAME-rich product phase is then routed to an existing Merox extractor tower for further purification by counter-current water wash (and drying). The crude glycerol co-product could either be recovered and sold or routed to another refining unit (such as FCC) for conversion by cracking. Another option is to install new equipment for glycerol purification. Since glycerol prices are expected to drop significantly as world-wide biodiesel production rates increase, the reuse of crude glycerol as a refinery feedstock may be more economically attractive than purification.

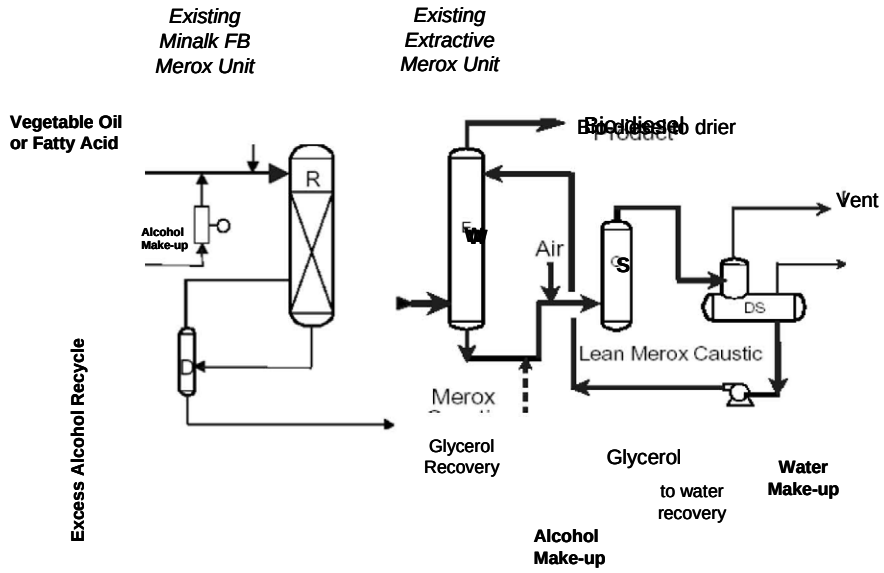


Figure 8. Possible Merox unit retrofit to FAME service.

MTBE Unit Retrofit

UOP MTBE units have been used by refiners for about 25 years to convert C_4 olefins from fluid catalytic cracking units (FCCs) to methyl tertiary butyl ether (MTBE). The process is somewhat analogous to a FAME production unit in that methanol is reacted with the feedstock to convert it to a fuel-blending component. Figure 9 illustrates one version of the MTBE flow scheme. While many MTBE units are still operating in refineries elsewhere, units located in US refineries are being shut down or revamped to alternate service due to new regulations prohibiting the addition of ethers to gasoline.

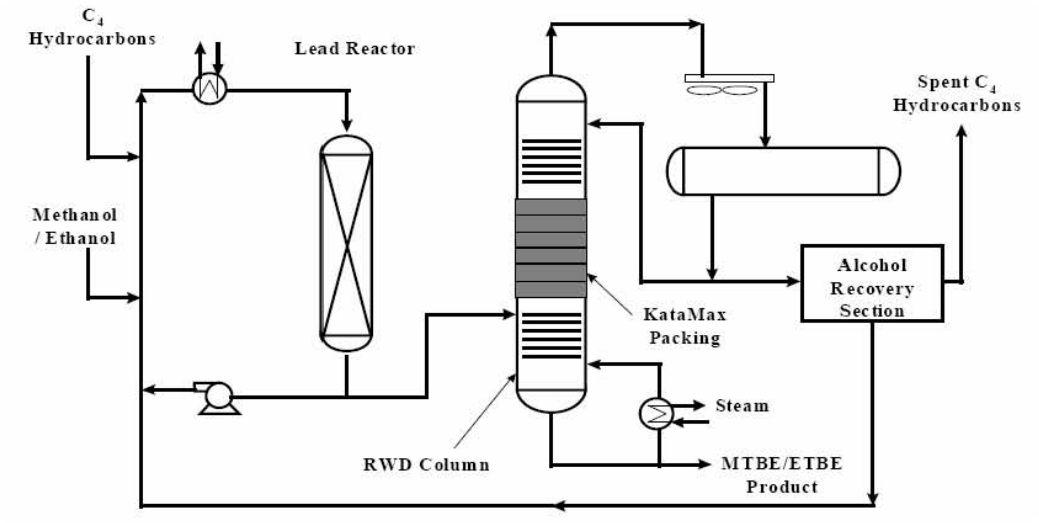


Figure 9. UOP MTBE (Ethermax) technology

A typical MTBE unit includes one or more fixed bed reactors where methanol (or ethanol) is reacted with butenes to form the corresponding ether. A portion of the reactor effluent is recycled to control the reactor exotherm. Unreacted feed components are separated from the higher-boiling ether product in a product fractionator. In Ethermax units, catalytic packing is used in the rectification section of the fractionating column to enhance conversion. Excess alcohol is then recovered and recycled back to the primary etherification reactor.

Retrofit of existing MTBE fixed-bed reactors to trans-esterify triglycerides in the presence of excess methanol also requires that a heterogeneous catalyst be developed. To ensure adequate mixing of the triglyceride and methanol in the reactor, either a pre-mixer and/or co-solvent would be used. The existing fractionation section would have to be modified to separate the higher boiling point FAME and glycerol products. However, it is expected that existing alcohol recovery equipment could be reused in biodiesel service.

III.1.2 Retrofit Enablers

The economic viability of retrofitting existing equipment for FAME production from biofeedstocks is highly dependent upon identifying a heterogeneous catalyst that can achieve high single-pass conversion under the normal reactor operating conditions of existing units ($<100^0$C). Because a typical FAME production unit has a relatively low processing capacity compared to most existing Merox or MTBE units, the unit turndown needs to be evaluated on a case-by-case basis. In principle, excess processing capacity can be judiciously used to provide longer reaction and/or separation times and to enhance high one-pass conversions of triglycerides.

Preliminary Heterogeneous Catalyst Study

There are incentives for development of a heterogeneous catalyst for FAME production whether it is employed in an existing or new unit:

- reduce operating costs (specifically consumption of chemicals)
- simplify product purification (eliminate caustic, acid, and salt byproducts)
- reduce generation of unwanted byproducts (soap stocks, wastewater, etc.)
- produce a more valuable glycerol product

Preliminary economic analyses suggest that cash cost of FAME production can be reduced by ~5% or more with the development of a heterogeneous catalyst.

A series of small-scale batch autoclave tests was performed to screen potential catalyst candidates using refined soy bean oil feedstock purchased from Aldrich and methanol. For each experiment, methanol, vegetable oil and catalyst were added to the autoclave in a prescribed ratio after which the vessel was sealed, heated to reaction temperature and stirred for a prescribed amount of time. In some cases, a co-solvent was added to ensure good contacting between the liquid phases. Afterwards, the products were phase-separated, excess methanol and co-solvent was removed and the oil phase was sent for analyses. A summary of operating conditions and analyses of the oil product from these tests is summarized in Table 2.

Table 2. Summary of FAME experimental results.

				<---Glyceride Compounds --->				
T & t	Run	CoSolvent	Catalyst	FAME	MONO	DI	TRI	Glycerol
55C, 2 hrs	486	Yes	A1	0.18	0.01	0.68	99.13	0.01
55C, 2 hrs	487	Yes	A1	0.05	<0.01	1.09	98.86	<0.01
80 C. 4 hrs	496	Yes	A2	0.08	0.01	0.77	99.14	<0.01
80 C. 4 hrs	496	Yes	A3	0.08	0.01	0.77	99.14	<0.01
55 C. 2 hrs	481	Yes	I1	0.6	0.04	1.62	97.74	0.00
55 C. 2 hrs	482	Yes	I2	0.01	0.10	1.73	98.16	<0.01
80 C. 4 hrs	497	Yes	I3	0.65	0.04	1.89	97.42	<0.01
80 C. 4 hrs	495	Yes	B1	3.08	0.36	6.44	90.12	<0.01
55C, 2 hrs	489	Yes	C1	6.58	1.09	12.43	79.87	0.03
55C, 2 hrs	493	No	C2	22.82	0.51	6.73	69.87	0.07
55C, 2 hrs	484	No	M1	54.73	0.79	6.37	37.62	0.49
55C, 2 hrs	485	Yes	M1	77.28	6.74	6.96	8.72	0.29
80C, 4 hrs	490	Yes	M1	86.32	5.18	4.45	3.45	0.60
80C, 4hrs	491	Yes	M1	10.63	1.01	9.96	78.36	0.04
55C, 4 hrs	492	Yes	AM1	31.44	0.53	4.23	63.53	0.27
60C, 4 hrs	498	Yes	AM1	31.97	0.27	3.43	64.1	0.23
			Solid	<---Glyceride Compounds --->				
T & t	Run	CoSolvent	Catalyst	FAME	MONO	DI	TRI	Glycerol
80 C, 4 hrs	500	Yes	B2	0.02	0.01	0.67	99.31	0.01
80 C, 4 hrs	501	Yes	B3	2.61	0.14	9.0	88.25	0.01
80 C, 4 hrs	502	Yes	B4	97.78	1.35	0.72	0.06	0.09
80 C, 4 hrs	503	Yes	B5	97.45	1.62	0.67	0.01	0.26
80 C, 4 hrs	509	No	B5	97.48	0.88	0.6	0.04	1.04
80 C, 4 hrs	511	Yes	B6	96.70	2.33	0.86	0.01	0.11
80 C, 4 hrs	506	Yes	B7	81.63	8.45	8.31	1.07	0.54
80 C, 4 hrs	507	Yes	B8	73.71	5.22	14.91	5.75	0.41

Several catalyst formulations (M1 and B4-B8) showed high one pass conversion of triglyceride to FAME at mild operating conditions (<100^0C). These catalysts all require further development to ensure that the high activity can be maintained under the expected continuous flow conditions associated with a commercial processing environment.

Financial Incentives For Retrofits

There are additional financial incentives associated with retrofitting existing refining equipment such as Merox and MTBE units to FAME production, including:

- leveraging existing land and refinery infrastructure,
- reducing capital investment for processing equipment, and
- capturing subsidies associated with production of renewable fuels.

However, the metallurgy of the existing equipment (typically carbon steel) may limit the processing of high free fatty acid (FFA) feedstocks. Preliminary economic analyses suggest that it is possible to reduce the overall investment requirements by 50% or more. Coupling the lower capital expenditures with renewable fuel subsidies make the potential payback on new capital reasonably short (<2 years).

III.1.3 Conclusions

In this preliminary analysis, potential retrofits of existing Merox and MTBE units to FAME production appear promising under the right circumstances:

- a heterogeneous catalyst is developed for operation under mild conditions (<100^0C)
- an appropriate combination of feed price, feed availability, and product market.
- adequate metallurgy for the proposed feedstock in the existing unit

Several promising heterogeneous catalysts were identified in UOP's laboratory screening test. However, the screening test only evaluates initial catalyst activity. The next step is to subject the most promising candidates to continuous-flow testing at operating conditions consistent with the anticipated commercial processing environment to ensure the high activity can be maintained.

It should be noted that for all the biodiesel catalysts that achieved high conversion, it was discovered that base had leached into the liquid phase so these tests were not completely heterogeneous but had a homogenous component as well. When the leachable base was removed from the catalyst with highest conversion, the conversion was much lower (less than 50%). Therefore further work to obtain a stable base catalyst will be needed in order to commercialize this process.

Assuming that an acceptable catalyst formulation is identified, then a realistic set of assumptions for plant capacity, feedstock cost, feedstock quality and product requirements need to be identified as the basis for a more detailed feasibility study.

III.2 GREEN DIESEL PRODUCTION

"Green diesel" refers to an acceptable diesel pool blend component produced from a suitable biofeedstock. In contrast to biodiesel discussed in Section III.1, green diesel hydrocarbons do not contain oxygen in their molecular structure. Biofeedstocks that are of particular interest for green diesel production are plant oils and greases.

III.2.1 Green Diesel Production Approaches

Two alternatives were evaluated for producing green diesel from biofeedstocks, illustrated in Figure 10:

- (a) co-processing oil or grease in an existing hydroprocessing unit, and
- (b) processing oil or grease in a standalone process unit.

The two case studies are summarized in Sections III.2.2 and III.2.3, respectively. Supporting experiments are summarized in Section III.2.4.

III.2.2 Green Diesel Production – Co-Processing Biofeedstocks in an Existing Unit

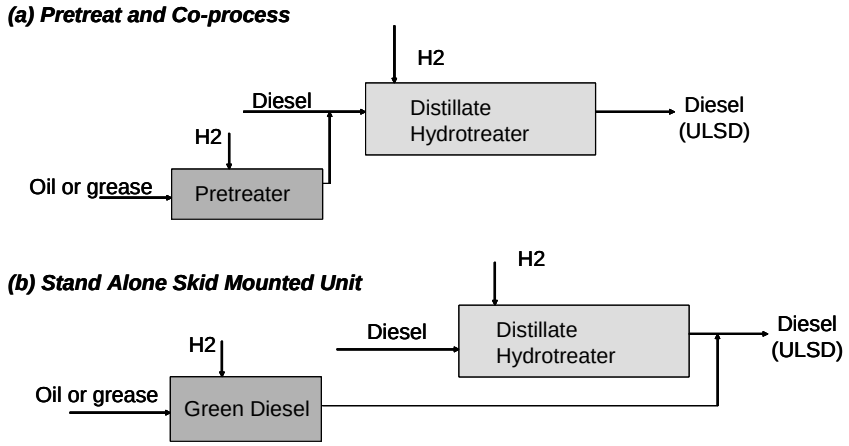


Figure 10. Alternatives for green diesel production.

The process unit for the biofeedstock co-processing a biomass source was a distillate hydrotreater for ultra-low sulfur diesel (ULSD). The base case was a hydrotreating unit with the following specifications:

- straight-run diesel feed from a blend of Middle-East crudes with less than 10% FCC light cycle oil
- 35,000 bpd, 950 psig separator pressure, 1.1 LHSV, and 6,000 scfb total gas rate
- chemical hydrogen consumption of 1.1wt.% relative to fresh feed
- heat release of 160 Btu/lb
- 30 month cycle time with a state-of-the-art Co/Mo catalyst.
- activity limited catalyst cycle with a catalyst temperature cycle of 27°F.

Table 3. Hydrotreating yields for brown grease.

Components	Wt%
Feeds	
Brown grease	100
H_2	2.9
Products	
$H_2S + NH_3$	0.04
C1 to C4	0.7
Naptha	2.4
CO_2	0.0
H_2O	12.7
nC17	0.0
nC18	87.2
Total	102.9

The objective of the co-processing case study was to produce a "G5" diesel pool in which 5% of the diesel pool contains "green diesel". Since the United States does not currently subsidize bio-diesel or green diesel production, the biomass source of choice is one with an inexpensive feed cost, such as brown grease with 100% free fatty acids. The hydroprocessing conditions are assumed to completely favor hydrodeoxygenation (HDO). In other words, oxygen in the biofeedstock is removed by reaction with hydrogen to form water and the C18 n-paraffin. For G5 diesel production at constant crude-based diesel feed rate, the biomass feed rate to the distillate hydrotreating unit must be approximately 5.8% of the crude feed rate, or 2050 bpd relative to the base case. In addition, the crude rate and crude slate are not changed to accompany the additional feed into the distillate hydrotreating unit. The estimated distillate yield is shown in Table 3. These yields assume no yield loss from production of light ends such as methane, ethane, LPG components, or naphtha.

Table 4 summarizes the expected hydrogen consumption and heat release for fatty acid components of the model brown grease, compared with the crude oil-based feed. Using the model brown grease composition shown in the third column, the estimated hydrogen consumption for hydrodeoxygenation is 3.0 wt%. The anticipated heat release is approximately 385 Btu/lb.

Table 4. Hydrotreating free fatty acids.

Feed	C:=	% in Model Feed	MW	n H2 / FFA	H2 Consumed (wt% feed)	Total Heat Release (Btu/lb)	Br No
Free Fatty Acid							
Stearic Acid	18:0	25	284.47	3	2.13	175	0
Oleic Acid	18:1	45	282.46	4	2.85	367	57
Linoleic Acid	18:2	25	280.44	5	3.59	562	114
Linolenic Acid	18:3	5	278.43	6	4.34	760	172
Diesel					1.08	160	2.5

The effects of the following factors on the start-of-run average bed temperature (activity) and deactivation rate were analyzed using UOP-proprietary distillate hydrotreating reactor correlations:

- properties of the brown grease feed such as sulfur, oxygen, and olefin content
- heat release from olefin saturation and hydrodeoxygenation of brown grease
- increased space velocity
- "treat-gas" ratio, or the total gas (makeup plus recycle gas) ratio

Three cases were analyzed to demonstrate the individual effects of the variables relative to the base case:

- Case I demonstrates the effect of brown grease feed properties. Case I is the base case with 5.8% biomass added to the fresh feed while maintaining the total fresh feed rate. The crude-based feed rate is reduced to approximately 33100 bpd and supplemented with 1900 bpd brown grease. The product contains approximately 5% green diesel, as desired.
- Case II demonstrates the effect of increasing space velocity to accompany the additional biomass feed. Case II maintains the ratio between the feed types of Case I and increases total fresh feed rate to maintain the feed rate of crude in the base case. The refinery crude slate and crude rate is not changed from the base case. The treat-gas ratio is maintained at the base-case ratio, under the assumption that the recycle gas compressor is not capacity-limited.
- Case III builds upon Case II by limiting the recycle gas compressor capacity to the base-case absolute capacity.

The results of analyzing the three cases of brown grease co-processing are depicted in Figure 11 through Figure 13; the results are expected to represent the general behavior of low or no-sulfur biofeedstocks such as plant oils and greases.

Figure 11 shows the effect of co-processing brown grease on the catalyst temperature cycle, defined as the end-of-run (EOR) peak temperature minus the SOR peak temperature. For the purpose of this study, the end-of-run peak temperature is fixed at the base-case value. Brown grease shows has an activity advantage regarding desulfurization. In this study, the start-of-run (SOR) average bed temperature (ABT) is reduced by approximately 2°F. However, the activity advantage is eroded by the heat release of brown grease, which is nearly 2-1/2 times higher than diesel. When the space velocity is increased in Case II, the corresponding increase in released heat raises the SOR ABT by approximately 3°F, consequently decreasing the catalyst temperature cycle. Capping the recycle gas compressor absolute capacity in Case III limits the system's ability to control the catalyst bed temperature rise and, hence, the catalyst SOR ABT increases further, decreasing the temperature cycle by almost 4°F relative to the base case temperature cycle of 27°F.

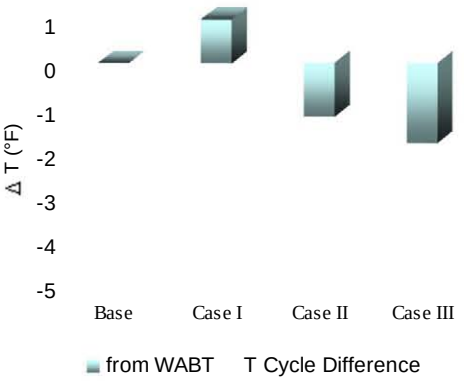


Figure 11. Effect of co-processing brown grease on catalyst temperature cycle.



Figure 12. Effect of co-processing brown grease on catalyst deactivation rate.

Figure 12 shows the relative deactivation rates for the cases analyzed. The sulfur content of the overall feed decreases when the crude-based feed is diluted with a biofeedstock containing little or no sulfur. The severity of the hydrotreating catalyst processing conditions is consequently reduced for the same product sulfur content. As a result, the deactivation rate decreases. As a consequence of further increasing the feed rate and decreasing the hydrogen circulation rate over the catalyst, the catalyst deactivation increases by approximately

20% over Case I. One important factor not included in this analysis of catalyst stability is water production.

The catalyst cycle length, shown in Figure 13, is determined by the temperature cycle and the deactivation rate. The cycle length for G5 diesel production, without decreasing the crude-based diesel rate or increasing the recycle gas compressor capacity, decreases by 6 to 7 months (Cases II and III). This reduced cycle time has economic consequences - for example, 2 to 3 days per year production loss and increased catalyst and associated turnaround costs.

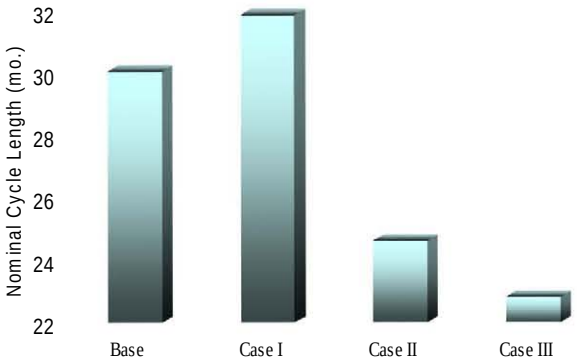


Figure 13. Effect of co-processing brown grease on catalyst cycle length.

The study also evaluated the impact of co-processing brown grease on reactor metallurgy and on the cloud point of the resulting diesel pool. The feed section metallurgy is carbon steel in hydroprocessing units such as hydrotreaters and hydrocrackers. There is a graduation of metallurgy from low-chrome through austenitic stainless steel in the combined feed exchangers. The fired heater tubes, reactor cladding and associated reactor circuit piping are typically 321 or 347 stainless steels. The Total Acid Numbers (TAN) of plant oils and greases range from 2 to 200. A TAN number of 0.5 to 0.6 is an industrially-accepted limit before considering upgrades to the process unit metallurgy. Therefore, the reactor section metallurgy of a hydroprocessing unit must be upgraded if any significant quantity of an economically-attractive biofeedstock is to be processed. The cost was estimated for upgrading the reactor section metallurgy to 317L stainless steel in the base case distillate hydrotreater and found to be substantial – approximately 7 to 8 million dollars. Additional capital costs that were not included are costs for brown grease tankage and brown grease pretreatment equipment for possible dewatering, acid washing, ion exchange, and/or desalting.

Distillates from brown grease and other similar biofeedstocks contain primarily n-paraffin. The n-paraffin content will decrease the cloud point of the diesel pool from 2 to 3°F per percent of n-paraffin content. Therefore, assuming that all diesel components in the diesel pool are hydrotreated to make ultra-low sulfur diesel, G5 diesel production may increase the cloud point of the diesel pool by 10 to 15°F. A diesel isomerization catalyst would be required to counteract the cloud point increase and preserve the green diesel molecules in the diesel pool. Unfortunately, such isomerization catalysts are typically noble metal catalysts and would require a two-stage hydroprocessing scheme, which is not typical for distillate hydrotreating units, necessitating major unit modifications.

In summary, co-processing of biomasses such as plant oils and greases in a typical refinery distillate hydrotreating unit has some drawbacks for green diesel production:

- The chemical nature of the biofeedstocks significantly increases hydrogen requirements under conditions that favor hydrodeoxygenation.
- The heat release from these feeds substantially reduces the catalyst cycle length.
- High TAN number feeds incur significant capital costs for metallurgy upgrading. Other capital costs may include feed pre-processing equipment to remove contaminants.

- Typical hydrotreating unit configurations do not permit remediation of increased cloud point due to n-paraffins in the green diesel component of the diesel pool.
- The process conditions for hydrotreating units for ultra-low sulfur diesel production favor HDO, producing water that may adversely affect catalyst performance.

In conclusion, standard refinery distillate hydrotreating units do not appear to be suitable for green diesel production in a co-processing scheme.

III.2.3 Green Diesel Production – Processing Biofeedstocks in a Stand-Alone Unit

Green diesel production in a standalone unit appears to address the issues identified in Section III.2.2 for co-processing schemes:

- catalyst performance can be improved through feed pretreatment
- a process can be designed to favor a different deoxygenation mechanism
- a simpler isomerization process can be used to prevent cloud point reduction
- the unit can be specifically designed to handle biofeedstocks

One possible flow scheme for a standalone unit is shown in Figure 14.

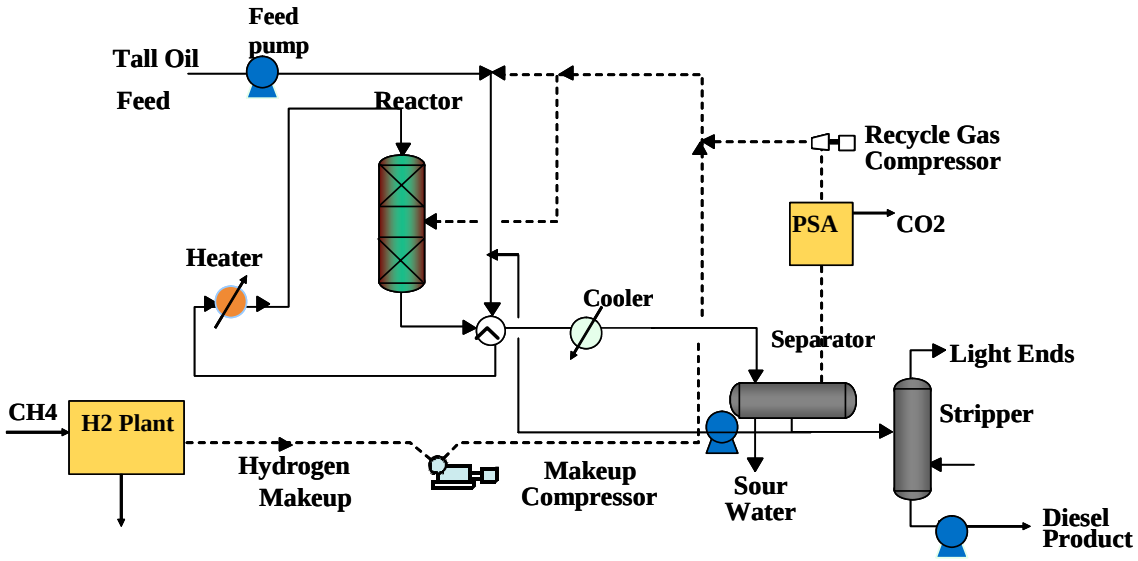


Figure 14. Proposed flow scheme for standalone production of green diesel.

Plant oils and yellow and brown greases may contain water, alkali metals (such as sodium, potassium), phosphorous, ash, and other contaminants. Metals permanently deactivate hydroprocessing catalysts. In a standalone unit, a pre-processing step would remove contaminants from the biofeedstock. using a combination of technologies such as hydrocyclones, desalting, acid washing, ion exchange, or fixed guard bed catalyst systems. This is a distinct advantage over

a co-processing system. A typical strategy for metals removal is to provide a less active sacrificial bed of hydrodemetallization (HDM) catalyst in front of the active hydrodesulfurization (HDS) catalyst. In existing distillate hydrotreaters, either active catalyst would be removed to load HDM catalyst or the metals would be allowed to deposit on the active HDS catalyst. Both choices would decrease the catalyst cycle length of an existing unit.

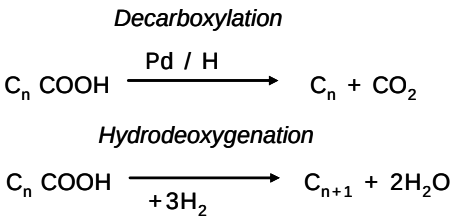


Figure 15. Decarboxylation vs Hydrodeoxgenation

The processing conditions to produce ultra-low sulfur diesel (ULSD) in an existing unit highly favor HDO, with the drawbacks outlined in Section III.2.2. An alternative mechanism, decarboxylation (DeCO2), removes oxygen in the biomass carboxyl groups as carbon dioxide instead of as water. In a standalone unit, catalyst and processing conditions can be selected to shift the oxygen removal mechanism from HDO to DeCO2. Decarboxylation and hydrodeoxygenation are illustrated in Figure 15.

Gas phase DeCO2 is discussed for several model compounds by Maier.[12] Table 5 compares the estimated yields of DeCO2 with HDO for the model brown grease. There are several clear advantages for DeCO2:

- Chemical hydrogen consumption is limited to olefin saturation, therefore significantly lower.
- Lower chemical hydrogen consumption reduces the hydrogen plant capital or hydrogen purchases and the makeup hydrogen compressor size.
- Water is not produced as a reaction product, thereby preserving catalyst performance.
- Rejected CO_2 can be captured in a relatively pure state as a product. From a greenhouse gas emissions viewpoint, the proposed green diesel process would not only be CO_2 neutral, but actually produce additional CO_2 credits.

Table 5. Hydrodeoxygenation versus decarboxylation theoretical yields

Components	DeCO2 Wt%	HDO Wt%
Feeds		
Brown grease	100	100
H_2	0.8	2.9
Products		
$H_2S + NH_3$	0.04	0.04
C1 to C4	0.6	0.7
Naptha	2.5	2.4
CO_2	15.5	0.0
H_2O	0	12.7
nC17	82.2	0.0
nC18	87.2	87.2
Total	100.8	102.9

Decarboxylation can not be considered in a unit producing ULSD for two reasons: (1) DeCO2 is favored over HDO at lower temperatures and pressures than the conditions required for deep desulfurization of traditional feedstocks; (2) the production of CO_2 will reduce hydrogen partial pressure unless the purge rate from the high-pressure separator, and subsequently, the make-up hydrogen rate are both increased. In a stand-alone unit, a pressure swing adsorption unit (PSA) system in the recycle gas stream can be provided to remove CO_2. In this way, recycle gas purge, recycle gas and makeup gas compression are minimized.

The relevant biofeedstocks have low concentrations of sulfur and nitrogen compounds relative to standard feedstocks. This makes n-paraffins in the green diesel product amenable to hydroisomerization without a true two-stage hydroprocessing unit such as would be required in a

co-processing scheme. A hydroisomerization reactor directly follows the olefin saturation / decarboxylation stage in the flow scheme of Figure 14.

A standalone unit can be design from the outset with metallurgy appropriate to the high TAN numbers of the candidate biofeedstocks. Upgrading most of the metallurgy to 317L stainless steel allows poorer quality and less expensive feeds (higher free fatty acid content) to be processed than would be possible in a typical hydroprocessing unit. However, the capital cost of the unit is obviously increased. Coupon testing must be done to determine whether the proposed metallurgy provides adequate corrosion protection. The estimated inside battery limits capital cost for a 2000 bpd standalone green diesel unit is approximately $6,000 to 7,000 per barrel.

III.2.4 Green Diesel Experimental Results

Background information on green diesel is available from Arbokem/Canmet, Fortum Oil, and most recently OMV. Arbokem has the key patent in green diesel production which expires in 2008.[13] Initially it was thought that yield estimates could be generated from literature and modeling results alone. Our initial yield estimates assumed that hydrodeoxygenation would be the primary mechanism for oxygen removal, as reported by Canmet/Arbokem from their initial studies[14] run at 700-2200 psi and 350-450C.

However, experiments performed in this project showed that both hydrodeoxygenation and decarboxylation occur, with the results summarized in Table 6. Decarboxylation is favored at lower pressures and hydrodeoxygenation increased with increasing pressure. Decarboxylation results in odd number paraffin production and CO_2 formation whereas hydrodeoxygenation results in even carbon number paraffin production; therefore the ratio of nC17 to nC18 is a measure of the DeCO2/HDO ratio. Standard hydrotreating catalysts of NiMo, CoMo and Pd all showed activity for both reactions. Furthermore it was demonstrated that the process could be run at lower temperatures than cited in the Arbokem patent and heavy material boiling above diesel range, which Arbokem produced, could be eliminated or reduced with proper choice of catalyst and conditions. Also, most experiments were done at 500psi which is well below the pressures cited in the Arbokem patent.

Table 6. Green diesel experimental summary.

	524	531	1316-C3	1316-C4
Feed	Vegetable oil	Vegetable oil	Vegetable oil	Vegetable oil
Catalyst	HCT (NiMo)	N200 (CoMo)	HCT (NiMo)	HCT (NiMo)
Test Unit	Autoclave	Autoclave	Plt 1316-B1	Plt 313-B1
WHSV	1.9	1.7	0.8	0.3
Temperature (C)	300-350	300-350	325	310
Pressure (psia)	500	500	500	500
Products				
% water	1.7	1.2	4.9	9.9
% $CO_2 + CO$	12.7	13.4	2.6	1.9
% Light HC	7.0	5.2	3.4	3.9
% diesel+	79	80	88.3	84
%heavy	0	3.2	0.3	0.3
%deoxygenation	90+	91+	85	99
nC17/nC18	3.0	2.1	0.6	0.49

Further testing is recommended to develop an optimized process. These experiments were proof-of-principle (POP) experiments, so good material balances were not achieved. In the autoclave, liquid and catalyst are charged to the reactor and H_2 gas is constantly flowing. For autoclave tests, losses are treated as gas which is calculated by difference so gas yield is overestimated and liquid yield underestimated. Gas composition changed throughout the test period because the test was not at steady state and true material balance and gas weights were not obtained.

The most active hydrotreating catalysts, such as UF-310 and UF-210 Stars, were not tested in these POP tests because of difficulties in presulfiding these materials. Therefore, there is considerable opportunity for improvement during development of a green diesel process, if pursued.

III.3 Comparison of Biodiesel and Green Diesel Process and Properties

It is useful to compare biodiesel and green diesel properties and process since they represent two different approaches for making diesel fuel from vegetable oil. Selected properties are compared in Table 7. Green diesel has excellent diesel fuel properties including an extremely high cetane number (see Section III.3). Cetane number is a measure of a diesel fuel's ignition delay, e.g. the time period between the start of injection and start of combustion of the fuel, and affects the price of both green diesel (80 cetane) and biodiesel (55 cetane). Biodiesel has lower heating value because of its oxygen content. Biodiesel also has other undesirable properties such as high density, and high NOx emissions. Overall, green diesel appears to be a superior product.

Table 7. Biodiesel and green diesel properties

	Biodiesel (FAME)	Green Diesel
%O	11	0
Density g/ml	0.883	0.78
Sulfur content	<10ppm	<10ppm
Heating Value (lower) MJ/kg	38	44
% change in NOx emission	+10	0 to -10
Cloud Point C	-5	-5 to -30
Distillation 10-90% pt	340-355	265-320
Cetane	50	80-90

Table 8 compares the processes by which biodiesel and green diesel are produced. The biodiesel process is fairly complicated, requiring multiple distillations and purifications. Green diesel is totally feed flexible and can handle low cost feedstocks like brown grease with high free fatty acid content without problems. Biodiesel requires methanol as feed and produces glycerol as a byproduct. Glycerol price is expected to drop significantly to $.10/lb as biodiesel production increases. Green diesel only requires hydrogen as a feed and produces only diesel and propane as a product so its value is not affected by methanol or glycerol price. Biodiesel requires a homogeneous catalyst, resulting in higher chemical costs.

Table 8. Comparison of biodiesel and green diesel production processes.

	Biodiesel	Green Diesel
Complexity	High-multistages	low
Feedstocks	Sensitive to level of FFA	No sensitivity to FFA
Requires	Methanol - 10%	H2 -2-3%
Byproduct	Glycerol	Propane
Catalyst	Homogeneous	Heterogeneous

As shown in Table 9, biodiesel does have an advantage in yields of diesel product per lb of vegetable oil feed. This is due to the fact that the oxygen in vegetable oil is retained in the biodiesel product where as the oxygen in vegetable oil is rejected green diesel as water or CO_2. However, the overall cost of biodiesel production is projected to be nearly twice that of green diesel.

Table 9. Green diesel and biodiesel yields.

Feed	Biodiesel	Green Diesel
% Oil or Grease	100	100
% H2		1.5-3.8
% methanol	8.7	
Products		
% water,CO2		12-16
% Lt HC		2-5
% diesel	96	83-86
% glycerol	12	
Operating cost $/gal	.05	.025

III.4 GREEN GASOLINE AND GREEN OLEFINS PRODUCTION

Vegetable oils and greases can be processed in an FCC to produce high yields of gasoline and oils. ACE microactivity tests were completed to determine the yields and product properties. The gasoline produced has high octane number and the vegetable oil produces a lot of high valued olefins at PetroFCC conditions (severe conditions design to maximize olefins production) compared to vacuum gas Oil (VGO), as shown in Table 10. The yields from processing vegetable oil and grease compared to VGO are shown in Table 10 and Table 11 .

Table 10. Green olefin yields.

	VGO	Vegetable Oil/Grease
C_2P+Methane	4.1	4.1
C_2=	8.6	8.7
C_3P	2.0	2.1
C_3=	22.0	22.4
C_4s	15.0	13.5
Gasoline	27.3	23.0
LCO	9.5	5.0
CSO	5.0	3.0
Coke	6.5	6.5
Water	0	11.7
RON of Gasoline	94.8	96.8

Table 11. Green gasoline yields

	VGO	Vegetable Oil/Grease
C_2=	1.5	1.9
C_3P	0.7	0.8
C_3=	4.0	4.6
C_4s	7.9	6.6
Gasoline	45.5	45.4
LCO	17.5	11.4
CSO	19.5	13.1
Coke	3.4	4.5
Water	0	11.7
RON of Gasoline	92.1	94.8

The acid number for typical total FCC product is 0.016. In one experiment, the acid number of the biofeedstock was 0.6 which is slightly elevated and raises concerns about corrosion. At a 5% level, however, the biofeedstock contribution would be only 0.03, and the net acid number would be 0.045, which is well below the problem where corrosion issues occur.

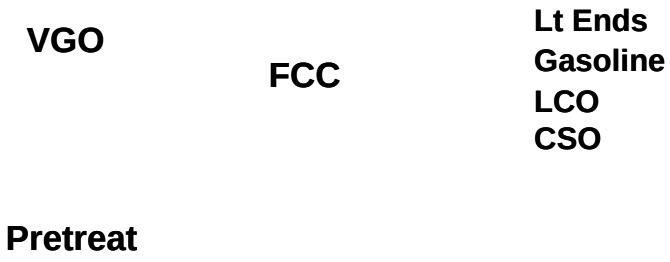


Figure 16. FCC processing approach.

In order to process vegetable oil and grease a separate feed system and pretreater would be best to remove metals (e,g, Ca,K) which would poison the FCC catalyst and to avoid metallurgy issues in the feed system when processing greases. A suggested processing scheme is shown in Figure 16.

III.5 Economic Assessment and Life Cycle Analysis

Economic comparisons for the various processing options are shown in Figure 17 and Figure 18. The cost estimate procedure has the following qualifications: These costs represent U.S.A. Gulf Coast erection to UOP standards for new equipment on a January 2005, open shop (non-union) labor basis. The equipment costs have an anticipated accuracy of -15%/+30%. The estimated erected cost (EEC) is a factored cost, which includes installation, associated bulk items (such as instruments, electrical, piping, and civil), indirects, and contractor's home office expenses. These costs are classified as inside battery limits (ISBL) for this estimate. The EEC is derived by multiplying the total equipment cost by a factor—the factor being obtained from an historical database which records average equipment cost versus total erected cost from previous detailed cost estimates developed by UOP Cost Estimating. The EEC has an anticipated accuracy of -30%/+50%. The EEC is for battery limits only. Indirect costs, home office expenses included in the EEC are not based on single equipment item installations; these equipment items are assumed to be part of a larger / typical refinery project.

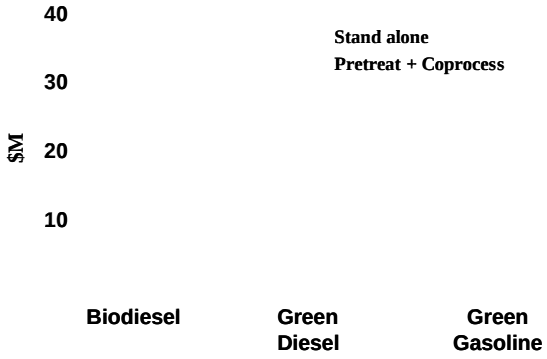


Figure 17. Capital costs of biofuels production from oils and greases.

Figure 18 summarizes the economic analysis of biofuels and chemicals production from oils and greases through comparison of their net present values (NPV). The NPVs of four products are shown as function of feedstock. Biodiesel is the least cost-competitive product for any feedstock, due to the high capital cost of biodiesel production.

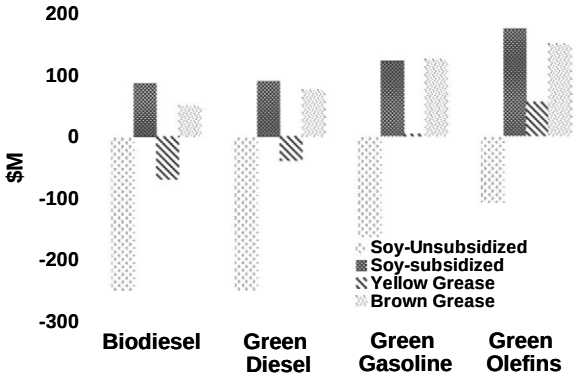


Figure 18. NPV comparison of biofuels and chemicals.

The effects of potential subsidies on NPV are illustrated in Figure 18.[15,16,17,18] Brown grease does not require subsidies to be an economically-viable feed for any of the products, because of its low cost. However, subsidies would have a significant impact on the viability of all soy-based products, as can be seen by comparing the NPV with and without subsidies. Note that only biodiesel is subsidized currently in the U.S, while all options are on equal footing in the EU.

A life-cycle analysis (LCA) of the various vegetable oil processing routes was conducted using the Simapro LCA program. LCA is a method to determine and compare the environmental impact of alternative products or processes "from cradle to grave". In this case, the scope of the analysis was from extraction through combustion. For analysis purposes, it was assumed that all fuels have the same performance in transportation use. In reality, biodiesel contains 12% oxygen and has much lower fuel efficiency than the other fuels; this effect is not reflected in the results. The primary focus of the analysis was on fossil energy consumption and emission of greenhouse gases, though other impact categories are included.

The results of the analysis are shown in Figure 19 and Figure 20. In general,, the green products have much lower total environmental impact score (Figure 19) and produce less CO_2 (Figure 20) than petroleum diesel. Of the biofuels, green diesel and green gasoline have the lowest environmental impacts and CO_2 production. The environmental impacts of biodiesel production are increased by the fact that it requires methanol which is produced from natural gas. Methanol production is a very energy-intensive process so it brings with it a strong environmental burden.

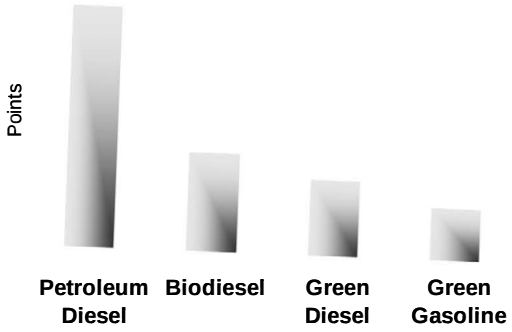


Figure 19. LCA – single environmental impact score .

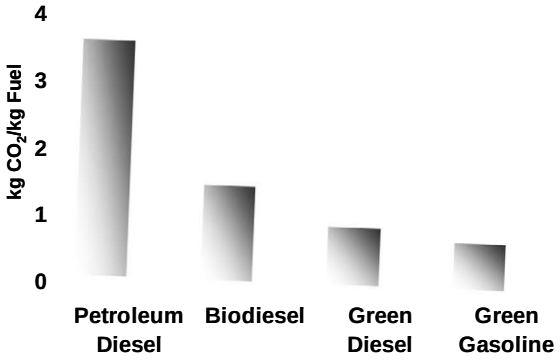


Figure 20. LCA –comparison of climate-active CO2

IV REFINERY OPPORTUNITIES FOR PYROLYSIS OIL

Pyrolysis oil, or bio-oil, is the material produced from pyrolysis of wood waste. Pyrolysis oil can be used as a substitute for fossil fuels to generate heat, power, and/or chemicals. Transportation fuels such as methanol and Fischer-Tropsch fuels can be derived from pyrolysis oil through synthesis gas processes. Pyrolysis oil is also a potential feedstock for hydrogen production. In addition, a wide range of chemicals can be extracted or derived from pyrolysis oil.

Section IV.1 outlines the properties of pyrolysis oil and alternatives for its utilization in refineries. This study investigated several processing options:

- Hydrotreating pyrolytic lignin to produce aromatics and gasoline (Section IV.2)
- Co-processing with vacuum gas oil (VGO) (Section IV.3)
- Aqueous Phase Reforming (APR) of water-soluble components to produce hydrogen (Section IV.4)

The study also investigated hydrothermal processing of pyrolysis oil and techniques for blending pyrolysis oil with other feedstocks (Section IV.5).

IV.1 BACKGROUND AND PROCESSING OPTIONS

The properties of pyrolysis oil depend on the specific feedstock and conditions of the production process, such as temperature, period of heating, ambient conditions, and the presence of oxygen, water and other gases. A typical process for producing pyrolysis oil is shown in Figure 21. Wood biomass such as sawdust, forest "slash", or wood waste from mills is ground to very small sizes and injected into a fluidized bed reactor. The fluidized bed typically consists of a circulating, non-catalytic material such as sand. The temperature and contact time are optimized to maximize liquid yields. Typical products from the pyrolysis process are gases, such as carbon oxides and light hydrocarbons like methane and ethane, and the pyrolysis oil itself, which consists of water-soluble oxygenated compounds and "pyrolytic lignin".

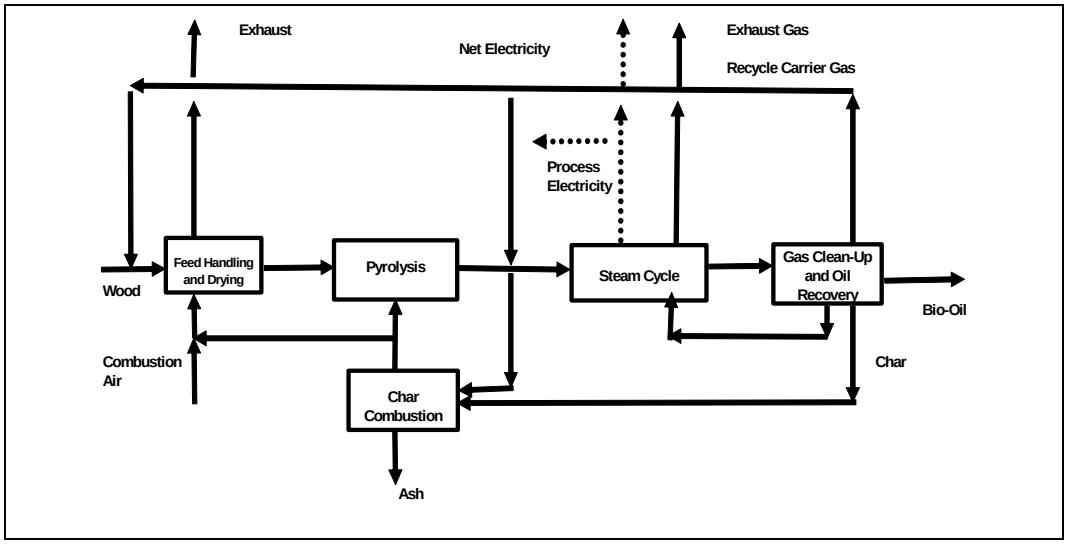


Figure 21. Typical pyrolysis process.

Table 12. Material balance for pyrolysis oil production.

Feed	
Biomass (forest waste, tpd)	2400
Product	
Pyrolysis Oil (tpd)	1440
Pyrolysis Oil (bpd)	7500
Capital Cost	$88 MM

The cost of pyrolysis oil is significantly affected by the high capital cost of the production complex. The economics of pyrolysis oil utilization could be improved by reducing these capital costs. The typical quantity of oil produced from forest waste in a pyrolysis unit is shown in Table 12.

Pyrolysis oil consists of an oil fraction, insoluble pyrolytic lignin, and a mixture of water-soluble components. The pyrolytic lignin is similar in structure to the lignin originating from the wood biomass, but has been reduced in molecular weight from the thermal conversion in the pyrolysis process. Pyrolytic lignin is much more hydrocarbon-like than the water-soluble pyrolysis oil since it has less oxygen. It is produced from the pyrolysis oil either by adding water to precipitate out the insoluble components or by gravity separation. Gravity separation yields more pyrolytic lignin and a higher water content. Pyrolytic lignin produced by gravity separation had a much high acidity than pyrolytic lignin produced by water precipitation. This suggests that acetic acid and other carboxylic acids are entrained in the pyrolytic lignin during gravity separation. The general properties of pyrolysis oil are summarized in Table 13.

Table 13. Pyrolysis oil properties.

	Pyrolysis Oil*	Pyrolytic Lignin	Water Soluble Pyrolysis Oil
Weight % MF	100	30.0	70.0
%C	44.7	64.2	36.3
%H	7.2	6.1	7.6
%N	.2	.3	0.16
%O	47.9	29.7	55.7
Acid Number	70 - 150	30 - 150	70 - 150
Heating value LHV Btu/lb	6,560	10,200	5,000

It is believed that the pyrolytic lignin is produced from thermal degradation of the lignin fraction of the biomass and therefore has essentially the same structure as lignin except a lower molecular weight. The structure of lignin is shown in Figure 22. It consists mostly of individual benzene rings connected via oxygen and short propane linkages. Breaking this structure at the oxygen linkages should yield aromatic gasoline and propane.

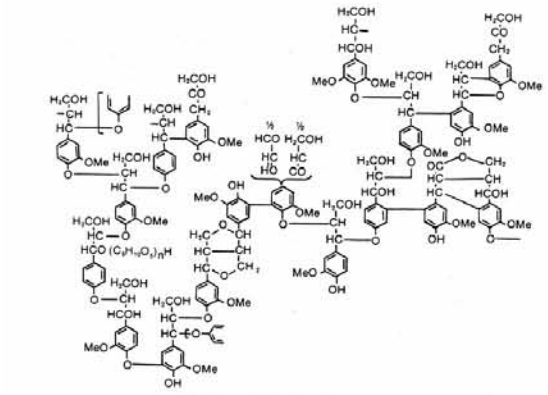


Figure 22. Structure of lignin.

The options for utilizing pyrolysis oil in refineries are affected by its high acid number, high water content, high oxygen content and high metal content, particularly potassium and calcium. Pyrolysis oil processing schemes for the refinery are shown in Figure 23.

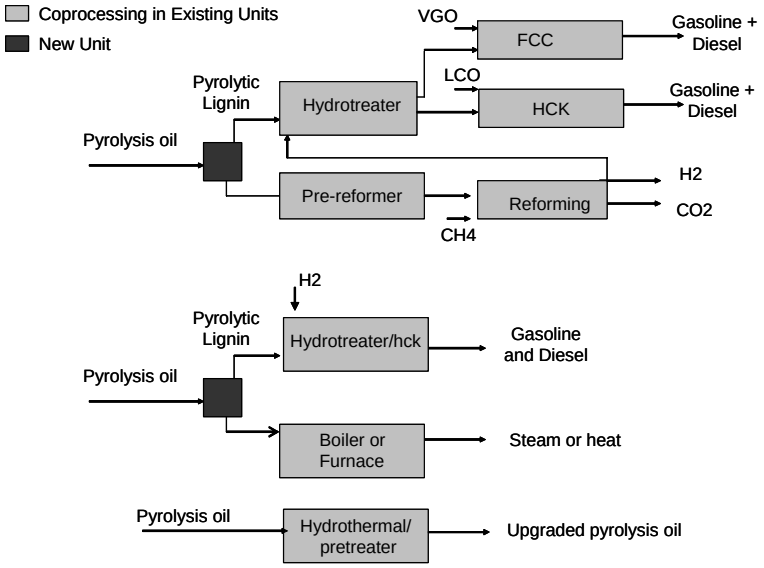


Figure 23. Pyrolysis oil processing routes.

Metals can be removed with guard beds or ion exchange. Metals removal is required before processing because these materials will typically poison catalysts. The high water content and very high oxygen content make it difficult to blend the pyrolysis oil with common refinery intermediate streams such as VGO. However it was found that proper additives can be used to form stable microemulsions. This is discussed more thoroughly in Section IV.3.

The most serious problem for pyrolysis oil processing is the high acid number of the pyrolysis oils which causes corrosion in standard refinery units. Pyrolysis oils can probably be processed using 317 stainless steel cladding, which is not standard in refinery units. Therefore pyrolysis oils require pre-processing in a 317 stainless steel system to reduce the acid number before processing in typical refinery units.

IV.2 GASOLINE AND AROMATICS PRODUCTION FROM PYROLYTIC LIGNIN

In previous studies, whole pyrolysis oil was hydrotreated at high pressures (2000 – 2500 psi) and low space velocities(0.1 – 0.2 LHSV). The resulting hydrotreated oil was then cracked in an FCC or hydrocracker to produce gasoline. At these high pressures and low space velocities, hydrodeoxygenation predominates. Large quantities of hydrogen are required to generate water during hydrodeoxygenation because of the high level of oxygen (46%) in pyrolysis oil. This approach is unlikely to be commercially viable because of the high hydrogen requirement and the high capital cost of the hydrotreatment step.

Because of its molecular structure, removing oxygen from pyrolytic lignin naturally generates materials in the gasoline boiling range. Pyrolytic lignin has a lower oxygen content than pyrolysis oil and therefore requires less hydrogen. Furthermore, decarboxylation is increasingly favored at lower pressure, which also reduces hydrogen consumption. Note that the same type of metal catalysts (Ni,Co,Pd,Pt) catalyze both reactions.

Two catalysts were tested for hydrotreating pyrolytic lignin:

- PNNL hydrotreated Dynamotive pyrolytic lignin using a Pd coated carbide catalyst in a continuous pilot plant.

- UOP hydrotreated Dynamotive pyrolytic lignin using a Ni-Mo catalyst in a batch autoclave.

The results are shown in Table 14. Both tests were successful at reducing the acid number, boiling point and oxygen content of the oil. The UOP catalyst appeared to be more active for oxygen removal at lower pressure and higher space velocity. Further tests will be required to optimize the process conditions and test the long term stability and activity of the UOP HCT catalyst (a newer-generation hydrotreating catalyst). However these tests suggest that pyrolytic lignin can hydrotreated under mild conditions, and that more active catalysts can be developed for this application to enable operation at higher space velocities and lower pressures.

Table 14. Results from hydrotreating pyrolytic lignin.

	PNNL HT	UOP HT
WHSV	0.52	1.0
LHSV	0.22	0.68
Catalyst	Pd/C	NiMo
Pressure	1900 – 2000	1500
Liquid yield %	55.6	40.8
% Oxygen removal	69	93
% Oxygen in product	19.5	5.9
Acid number of product	34	15
% Naphtha in liquid	30	60

The product from the PNNL hydrothermal test was then hydrocracked using a NiMo catalyst in a batch autoclave. The combination of hydrotreating and hydrocracking resulted in 96% oxygen removal and a very high level of conversion to gasoline, with the properties shown in Table 15. An even better process would use a more active catalyst in the hydrotreating step such as the HCT catalyst. It is likely that the aromatics production can be increased and of naphthene production reduced by further process and catalyst optimization.

Table 15. Hydrotreating+hydrocracking pyrolytic lignin.

	PNNL HT + HCK
LHSV, Step 1	0.22
LHSV, Step 2	1.5
Catalyst, Step 1	Pd/C
Catalyst, Step 2	Ni/Mo
Pressure, Step 1	1900 – 2000
Pressure, Step 2	1500
Liquid yield %	32.4
% Oxygen removal	96
% Naphtha in liquid	80

Estimates of the overall yield were developed for the overall two step process, based on the experimental results. These estimates, shown in Table 16, were used as a basis for economic calculations.

Table 16. Yield estimate for hydrotreating/hydrocracking pyrolytic lignin.

Feed	**Wt%**	**bpd**
Pyrolytic lignin	100	2250
H2	4 – 5	
Product		
Light ends	15	
Gasoline	30	1010
Diesel	8	250
Water, CO_2	51 – 52	

Commercially, hydrotreating and hydrocracking would be done in a single process unit with two catalyst vessels and intermediate water removal. However, since gravity-separated pyrolytic lignin has such a high acidity, hydrotreatment in vessels clad with 317 stainless steel would be required before coprocessing in existing hydroprocessing or hydrocracking units. The industry standard for refinery vessels is that the

total acid number of the blend must be less than 0.6. Therefore the TAN for the hydrotreated lignin product would have to drop below 6 for a 10% blend or below 12 for a 5% blend. This should be achievable with a more active catalyst in the first step.

The total quantities of gasoline produced and pyrolytic lignin processed is relatively small by refinery standards. After hydrotreating, which requires 317 SS, most of the lignin conversion and upgrading has been performed, so it will generally be more cost-effective to perform the entire process in a single new skid-mounted refinery unit (Figure 24). There are a few cases in which refinery hydrotreating/hydrocracking units have already been designed with 317 because they are processing high naphthenic acid crudes. These units would be ideal for processing pyrolytic lignin but are relatively rare.

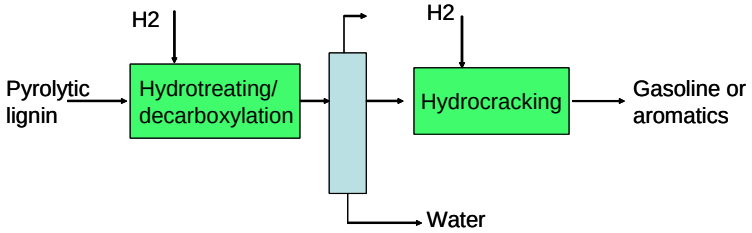


Figure 24. Process flow for hydrotreating/hydrocracking of pyrolytic lignin.

IV.3 COPROCESSING WITH VGO IN AN FCC

Small FCC pilot tests (ACE tests) were run to determine the crackability of pyrolysis oil blended with vacuum gas oil (VGO), pyrolytic lignin blended with VGO, and neat hydrotreated pyrolysis oil from PNNL. In the blends, the VGO serves as a hydrogen donor. Stable blends are needed for the pilot plant injector system although two separate feed systems and nozzles could be used in commercial units. Stable blends were prepared using Hypermer surfactants. Hypermer is a non-ionic polymeric surfactant made by Uniqema.[19]

The results are shown in Table 17. Compared to VGO, the pyrolysis oil, pryrolytic lignin and hydrotreated pyrolytic lignin tend to form high levels of coke. On an incremental basis, the pyrolysis oil formed 84% coke+water+COx and the lignin formed 70% coke +water+CO2 from the biofeeds. On an incremental basis the pyrolysis oil formed 16% coke and the pyrolytic lignin formed 27% coke. This is consistent with results reported on FCC cracking of neat pyrolysis oils

Table 17. Yields for FCC conversion of pyrolysis oil, pyrolytic lignin and HT pyrolysis oil.

	VGO	20%Pyrolysis oil 80%VGO blend)	20%Pyrolytic Lignin 80% VGO Blend	HT Pyrolytic Lignin (PNNL)
C_2-	2.0	3.3	3.6	3.8
C_3P	1.2	2.1	2.4	.7
C_3=	5.9	6.1	6.3	2.6
C4	11.1	13.5	14.3	2.7
Gasoline	42.7	40.6	41.3	28.8
LCO	14.8	9.1	9.7	15.6
CSO	18.5	4.8	4.7	6.2
coke	3.8	7.1	9.2	16.1
Water + CO_2	0	13.5	8.5	23.5

and the carbon residue results for the samples shown in Table 18.[20,21,22]

Table 18. Carbon residue results

	Carbon Residue Test
Pyrolysis oil	21
Pyrolytic lignin	27-29
Hydrotreated pyrolysis oil (HT82)	6.7

For the blends of VGO with pyrolysis oil or pyrolytic lignin, the acid bio-oils appeared to increase the crackability of the VGO and shift VGO yields toward increased light ends and lower LCO and CSO which is an economically attractive outcome. The neat hydrotreated lignin (HT-82) had unexpectedly high coke levels. Any follow-up tests should test blends of the hydrotreated lignin with VGO to determine whether any synergies exist for blending this material with VGO. VGO and hydrotreated lignin form stable blends without need for surfactant. The high levels of coke obtained with 20% blends would be unacceptable for most FCC units but 5% blends might be possible. Further testing of 5% blends would be required to determine the viability of this approach. The properties of full boiling range liquid samples produced from the pilot plant test are shown in Table 19.

Table 19. Product properties of total liquid products from FCC testing at 1000F and 5/1 cat/oil ratio

	80% VGO and 20% pyrolytic lignin	Hydrotreated pyrolytic lignin
%C	88.6	89.5
%H	9.3	9.5
%O	.38	.56

As an alternative to blending, coprocessing pyrolytic lignin and pyrolysis oil with VGO in an FCC might be possible if a separate feed system were used to inject the pyrolysis oil or pyrolytic lignin. There are three concerns which would need to be addressed in order to determine the viability of this approach:

- Would the metallurgy of the FCC riser system be affected by injecting highly acid material or would the material react quickly enough to avoid problems?
- Would any acidic or other undesirable products be formed that would adversely affect the liquid product quality and downstream processing?
- Would any acid materials be formed which would cause corrosion of downstream recovery equipment?

Co-injection of pyrolytic lignin in an FCC would be possible if the lignin was separated via water precipitation to keep the acid number below 35. The FCC is typically the largest unit in the refinery and so the lignin will be diluted to about 1.5% pyrolytic lignin in the VGO feed. For a 50,000 bpd unit (typical for an average 150,000 bpd refinery) this would only allow 750 bpd of pyrolytic lignin in the feed. For a large 100,000 bpd FCC, 1500 bpd of pyrolytic lignin could be processed. Co-injection would also be possible if the pyrolytic lignin was previously hydrotreated to reduce the acid number. Since the FCC is the biggest unit and the heart of most refineries, much more development work would be required to minimize refiner risk before such an approach would be viable.

IV.4 H2 PRODUCTION FROM PYROLYSIS OIL

Pyrolytic lignin is deficient in hydrogen, making this portion of pyrolysis oil a poor feed for reforming into hydrogen. On the other hand, the organic compounds in the water-soluble phase are suitable for transformation into hydrogen. Table 20 shows the nominal composition used for the water-soluble phase organics on a moisture-free basis.

Table 20. Composition of aqueous-phase compounds from pyrolysis oil

Component	Wt%
Glyoxal	10
Formic acid	14
Hydroxyacetaldehyde	17
Acetic acid	17
Ethylene Glycol	2
Acetol	5
Sugars and sugar anhydrides	35

The following properties of the water-soluble phase of the pyrolysis oil must be considered in a H_2-production process:

- The hydrogen content of the aqueous-phase organic compounds is substantially lower than that of typical hydrogen reforming feeds such as methane, LPG or naphtha.
- The organic compounds for reforming are in a water solution.
- The water-soluble phase consists of organic acids such as formic and acetic acids, with implications for processing unit metallurgy.
- Higher molecular weight carbohydrates such as sugars and anhydro-sugars are likely to carbonize to tar or char while preheating to typical reforming temperatures.

There are several technologies for converting hydrocarbons and biomasses into hydrogen. However, steam reforming is the primary technology for hydrogen generation in refineries and therefore the focus of the analysis of integrating pyrolysis oil into refining for hydrogen production (IV.4.1). The Aqueous Phase Reforming (APR) technology offered by Virent Energy Systems may be an alternate technology but most likely would be implemented in a stand-alone unit (Section IV.4.2).

IV.4.1 Integration of Pyrolysis Oil Reforming into Refinery Hydrogen Plants

The pyrolysis oil production basis for this study is 7500 bpd of pyrolysis oil. The aqueous phase is 70 lv% of the pyrolysis oil including water. The aqueous phase includes 30 lv% water. Therefore, approximately 3650bpd (60500lb/h) of aqueous phase components on a moisture free basis is available for reforming to hydrogen.

Table 21. Pre-reformer syngas composition for the aqueous phase of pyrolysis oil.

Component	Composition (wt%)
Sugars and Sugar Anhydrides	35.4
Glyoxal	10.3
Hydroxyacetaldehyde	16.9
Formic Acid	14.1
Acetic Acid	16.5
Ethylene Glycol	2.3
Acetol	4.5

Adiabatic pre-reforming is the technology of choice to integrate reforming of the aqueous phase of pyrolysis oil into an existing hydrogen plant. For the nominal composition shown in Table 20 and assuming equilibrium at the reactor outlet, the resulting pre-reformer synthesis gas composition is found in Table 21. Figure 25 shows the proposed process flow scheme. The pre-reformer is an adiabatic fixed bed reactor operating at relatively low temperatures. Superheated steam is mixed with the preheated aqueous phase to produce a steam-oxygenates ratio of 1:1 (mass/mass). The preheated aqueous phase is mixed with the superheated steam as close as possible to the catalyst bed. Steam reforming, shift-gas and

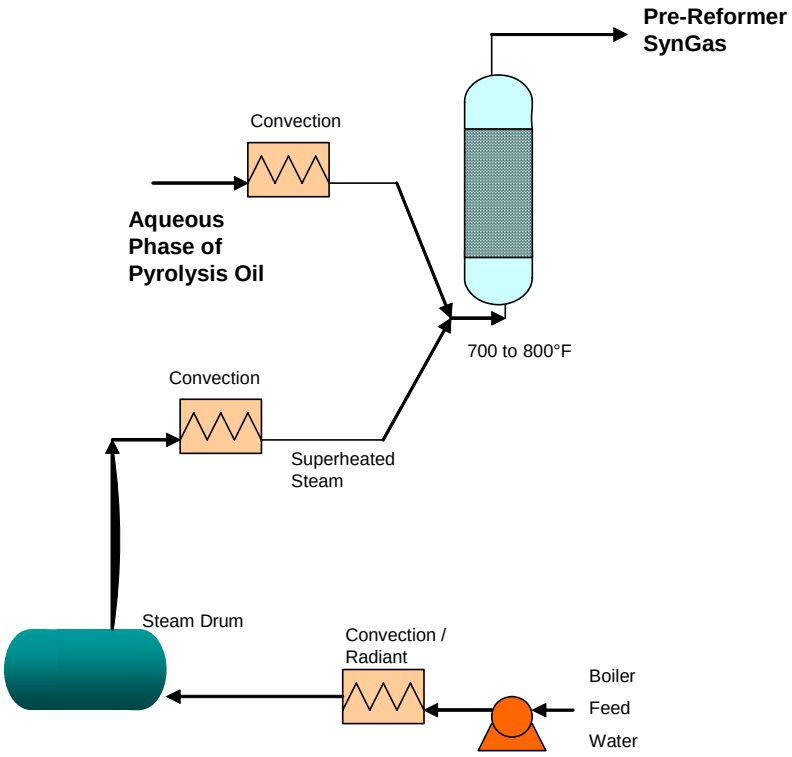


Figure 25. Adiabatic pre-reformer for the aqueous-phase of pyrolysis oil.

methanation reactions occur in the adiabatic pre-reforming catalyst. Overall, the pre-reforming is highly exothermic for the aqueous phase composition. The pre-reformer synthesis gas is delivered without heat integration directly to the main steam reforming reactor.

Based on the acidity of the feed, 317L stainless steel is the proposed metallurgy for the feed pump, fired heater, reactor cladding and associated piping and valves. The installed inside battery limits capital cost is approximately $15 to 20 MM, or $5500/bbl feed.

Two cases were compared:

- Case I - Hydrogen production from steam reforming of methane alone for the base refinery hydrogen production rate, 25MM scfd.
- Case II - Reforming of the target quantity of the pyrolysis oil aqueous phase with adiabatic pre-reforming – 3650 bpd, 60,500 lb/h. Natural gas is supplemented in the main steam reforming plant as required to produce the baseline quantity of hydrogen. The steam to feed ratio is varied to observe the effect on H_2 production and utility requirements. The effect on reforming catalyst stability is not addressed for the decreasing steam ratios.

The analysis determined that the natural gas feed to the SMR reactor section can be completely displaced with the aqueous phase of the pyrolysis oil to produce at least the baseline H_2 generation rate of 25 MMscfd. The CO_2 emission per unit of hydrogen production is reduced by approximately 50 to 65% because components in the aqueous phase of the pyrolysis oil do not contribute to CO_2 emissions while all carbon in the natural gas feed for SMR is eventually emitted as CO_2.

The hydrogen COP is approximately 50% higher for integrated adiabatic reforming of the aqueous phase of pyrolysis oil than for SMR. Feed costs represent two-thirds of the hydrogen COP and almost the entire COP for SMR. The projected decrease in CO_2 emission per unit of hydrogen is not sufficient to make up the difference through CO_2 credits. The delivered cost of pyrolysis oil must be reduced for this process to be competitive with SMR.

IV.4.2 Aqueous Phase Reforming (APR) of the Aqueous Phase of Pyrolysis Oil

The Aqueous Phase Reforming (APR) process is a concept patented by Virent Energy Systems. A parametric simulation study was performed examining the effects of reaction temperature and pressure on hydrogen generation and cost of production for APR of pyrolysis oil with the composition shown in Table 20. The ranges of temperature and pressure of interest were those cited by the patent and other public literature from Virent Energy Systems: 350 to 500°F and less than 1000 psia. APR was modeled with the PRSV thermodynamic property package in a process simulator using reforming equilibria for the reactions in Table 22. The effects of temperature and pressure on hydrogen generation indicate that the extent of reaction is favored by increasing temperature and pressure. Vaporization of the feed in the fired heater is energy intensive. Therefore, in this analysis, the upper limit of temperature was bounded by the saturated liquid temperature at a given pressure.

A proposed flow scheme for the APR process is shown in Figure 26. The aqueous phase of the pyrolysis oil and recycled water are heated up to reaction conditions through exchange with the reactor effluent and a fired heater. Pressure, temperature and the water recycle rate can be optimized to economically maximize the conversion to hydrogen. After exchanging heat with the reactor feed, the reactor effluent is cooled by an air cooler and the predominantly liquid recycle is separated from the synthesis gas. The synthesis gas is primarily composed of carbon oxides and hydrogen. A Pressure Swing Adsorption (PSA) unit is used to purify the H_2 and reject a tail gas.

Table 22. Reforming equilibrium reactions for APR of pyrolysis oil components

Component Reforming	Equilibrium Reaction
Acetic Acid Reforming	$CH_3(COOH) = 2\ H_2 + 2\ CO$
Acetol Reforming	$CH_3(CO)CH_2OH = 4\ H_2 + 3\ CO$
Ethylene Glycol Reforming	$H_2C(OH)C(OH)H_2 = 3\ H_2 + 2\ CO$
Formic Acid Reforming	$H(COOH) = H_2O + CO$
Glyoxal Reforming	$H(CO)(CO)H = H_2 + 2\ CO$
Hydroxyacetaldehyde Reforming	$H_2C(OH)(CO)H = 2\ H_2 + 2\ CO$
Sugar Reforming	$C_6H_{12}O_6 = 6\ H_2 + 6\ CO$
Water Gas Shift	$CO + H_2O = H_2 + CO_2$

Process modeling suggests that part of the plant will be exposed to hot acetic vapor which poses metallurgical challenges. The corrosivity of acetic acid solutions (and other organic acids like formic acid) is very dependent on process conditions and existing contaminants. 316 SS may not be an acceptable metal of design for boiling acetic acid solutions at concentrations of 10% or higher. Copper or alloys of copper and nickel may be viable alternatives, especially in oxygen-free environments, unless the material is transferred from tankage where oxygen content is a real concern. Development of a commercial APR process will require corrosion testing at the various process conditions found throughout the process.

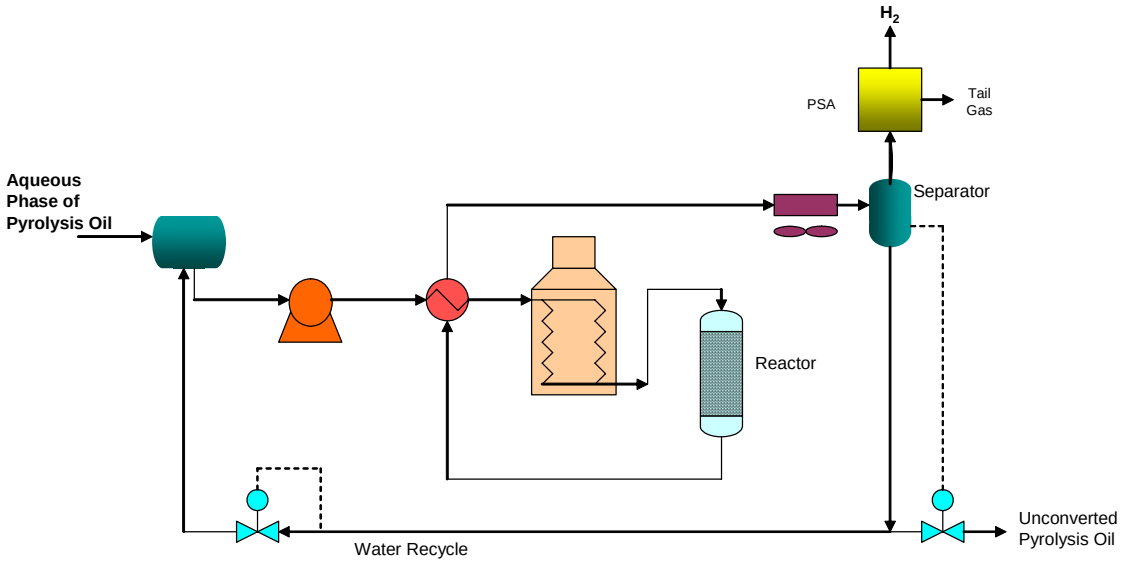


Figure 26. Proposed APR process flow scheme.

The most conservative approach is to use titanium Grade-II clad carbon steel. The difference in erected cost between Ti-clad and 316SS is surprisingly small - within 5%. The total installed inside battery limits capital cost is approximately $65 MM for the APR plant based on the proposed flow scheme and the baseline hydrogen production rate of 25 MMscfd.

The hydrogen COP from pyrolysis oil aqueous phase reforming is appreciably higher than SMR. Alternate design concepts were considered to increase economic feasibility by reducing capital investment and COP. The most promising is similar to the flow scheme of Figure 26, but without liquid recycle. A summary of the COP and estimated capital costs comparing the initially proposed flow scheme and the low acetic-acid conversion alternative are presented in Table 23, assuming $16/bbl for pyrolysis oil. The process results in low acetic acid conversion and includes recovery of the acetic acid as a net product. Two distillation columns could be used for acetic acid recovery. Waste water and non-condensable light ends are vented overhead in the first column. Purified acetic acid is recovered in the overhead of the second column; tar or other heavier by-products are removed in the bottoms. With elimination of recycle and assuming efficient oxygenate reforming of the feed pyrolysis oil, the COP can be reduced to approximately $0.48/lb, which includes acetic acid fractionation utilities. Acetic acid fractionation costs are approximately $0.06/lb H_2 generated.

Table 23. Comparison of APR process flow schemes.

Process Concept	COP ($/lb H_2)	EEC (MM $US)
Preliminary Process Design – complete acetic acid conversion process	0.65	65
Low acetic acid conversion process	0.48	10

Table 24 compares the capital costs and production capacity for the three routes to generate hydrogen from the water-soluble portion of pyrolysis oil: steam methane reforming, partial oxidation and liquid phase reforming. All are based on 7,500 bpd pyrolysis oil feed that has been separated into the lignin and water-soluble fractions.

Table 24. Comparison of H_2 production routes.

	EEC Capital Cost ($MM)	Production Capacity (MMSCFD)
Steam reforming	24	28.7
Partial oxidation	37	15.9
Liquid phase reforming	30	33.3

IV.5 HYDROTHERMAL PROCESSING AND BLENDING STUDIES

Supporting studies were conducted to investigate the potential for pretreating pyrolysis oil by hydrothermal processing and for improvements to pyrolysis oil blending properties.

Hydrothermal Processing

Hydrothermal processing is a simple pretreatment step which could be done in the field to reduce the costs of transporting pyrolysis oil by removing oxygen and reducing acidity. Batch autoclave tests were performed to hydrothermally process the pyrolytic lignin, pyrolysis oil and resid. In these tests, water is mixed with pyrolytic lignin and the mixture is heated up to 300 or 350 C. The pressure is maintained so that the mixture is kept in the liquid phase. The experimental conditions are shown in Table 25. The catalysts were cobalt and nickel compounds.

Table 25. Hydrothermal processing experiment conditions.

	Pyrolytic lignin,g	Resid g	Catalyst	Water,g	Temp C	Time min	Pres Psi (max)	Water phase,g	Organic phase	Gas,l	Gas,% CO2
1	75.7	0		75.1	300	15	1380	69.9	69.9	2.2	33
2	51.5	50.8		50.1	350	15	1530	5	131.2	2.2	12
3		76.6		75.2	350	15	2500	20.5	107.2		11
4	52.5	60.7		50.6	350	120	2480	28.6	106.6	2.9	24
5		75.7		75.0	350	120	2480	29.3	105.1	.03	6
6	77.8		Co	>76.7	350	20	2850		186 total	2.8	55
7	77.0		Ni	75.1	350	20	2800	77.0	46.5	3.3	47
8	75.1			75.3	300	15	2100?	74.3	59.5	2.1	27
9	75.0	76 (pitch)			250	15	480?		145	1.1	45

The resid did not appear to improve with hydrothermal treatment, but the pyrolytic lignin lost oxygen as shown in Table 26. Unfortunately the product from hydrothermal treatment became more viscous as well (>1500 MPas @ 95 C) and some char formation is reported in Runs 6,7and 8. Hydrotreatment under H_2 pressure breaks the molecules as the oxygen groups are removed, resulting in smaller molecules. Hydrothermal treatment does not have this effect and may result in polymerization of the molecules. As long as the aromatic rings have not condensed to form asphaltene structures, it may be possible to hydrocrack these materials to form aromatics in a hydrocracker. A key test would be to determine whether hydrothermally-treated pyrolytic lignin can be processed with LCO in a mild hydrocracker to produce aromatics. Since the hydrothermal process is a simple and relatively inexpensive option for pretreatment, more follow up work in this area is recommended.

Blending Studies

Table 26. Product properties of hydrothermally processed pyrolytic lignin.

	Pyrolytic lignin	Hydrothermally treated lignin
Process conditions		
Co-feed		50% water
Temp,C		300
Time		15 min
%C	56.67	79.1
%H	6.67	13.5
%O	26.6	7.1
%N		0.2
%water	11.7	

One of the big challenges with pyrolysis oils is the fact that they have limited solubility in typical hydrocarbon fractions and fuel products. Small amounts of materials can be extracted from pyrolysis oils into hydrocarbon phases but blending studies are difficult because the pyrolytic lignin or other heavy fractions of pyrolysis oils tend to coat onto beakers and equipment leading to poor material balance. Therefore to be conservative, only increases in the petroleum fraction phase (VGO or LCO) are counted as extracted material. Roughly 3% pyrolytic lignin was extracted into LCO (light cycle oil) in blending tests and roughly 6% pyrolysis oil could be extracted into VGO when water was added to the pyrolysis oil phase.

However it was found that stable microemulsions of 20% pyrolysis oil or 20% pryolytic lignin in VGO or LCO could be formed when 1% Hypermer 2296 and 1% Hypermer 256SF surfactants were used. Also encouraging was the fact that the HT-82 sample of hydrotreated pyrolytic lignin was very soluble in both VGO and LCO.

IV.6 Economic Analysis of Pyrolysis Oil Processing Options

Table 27 shows that pyrolysis oil is intermediate in cost between heavy residual oil and natural gas on a $/MMBTU basis. Refiners could burn pyrolysis oil in furnaces designed for heavy fuel oil that have been shifted to natural gas to minimize SO_2 emissions. This would also allow refiners to reduce CO_2 emissions from boilers and fired heaters and obtain a CO_2 credit. This is an immediate application for refiners and other industries using natural gas to minimize pollution. Minor capital investment would probably be needed to change burner tips and modify boilers to allow co-firing of natural gas and pyrolysis oil. It would be worth $5.6 MM/year to substitute 5250 bbl/d of water soluble pyrolysis oil for natural gas in furnaces or boilers or $7.4 MM/year to substitute 5250 bbl/d of pyrolysis oil itself.

Table 27. Fuel value of pyrolysis oil.

	$/MMBTU
Heavy Fuel Oil	4.2
Natural Gas	6
Pyrolysis Oil	4.7

The baseline 5250 bpd of pyrolysis oil aqueous phase contains 3650 bpd water-soluble components on moisture free (m.f.) basis. Assuming the nominal composition in Table 20, the mass rate is 65,940 lb/h and the lower heating value of the m.f. organics is approximately 5600 Btu/lb. The water in this stream has no net heat value.

To raise 1600 psig, 700°F VHP superheated steam from ambient temperature boiler feed water requires 1.3 MMBtu per 1000lb steam. Therefore, burning the aqueous phase generates 370MMBtu/h on a 100% efficiency basis. The efficiency basis is valid if the aqueous phase of the pyrolysis oil provides supplemental firing for the heat recovery-steam generation (HRSG) section of a cogeneration facility. Otherwise, 85 to 90% efficiency in a stand-alone boiler would be more appropriate. The amount of VHP superheated steam generated will be approximately 250,000 to 285,000 lb/h. The steam generated is adequate for power generation or the steam could be generated at HP steam levels to drive 1 or 2 large refinery condensing turbines.

The economics for producing gasoline from pyrolytic lignin are shown in Table 28, assuming $18/bbl pyrolysis oil ($16/bbl +$2/bbl transportation charges) and $40/bbl crude. The incentives total to 4 MM/year.

Table 28. Incentives for gasoline production from pyrolytic lignin.

	$/D	Quantities
Feed		
Pyrolytic lignin	40,500	2250 bpd
H2	25,680	21.4 tpd
Product		
Light ends	19,903d	64 tpd
Gasoline	52,520	1,010 bpd
Diesel	12,000	250 bpd
Utilities	-4,800	
Incentive	12,843	

The capital cost for a hydrotreating/hydrocracking unit producing 1,010 bpd of gasoline is $30 MM. Producing gasoline from pyrolytic lignin becomes economically attractive for $18/bbl pyrolysis oil at a crude price of $50/bbl. As pyrolysis oil price decreases, producing gasoline from pyrolytic lignin becomes attractive at lower crude oil prices, illustrated in Figure 27 .There is a strong sensitivity to pyrolysis oil price at $40/bbl crude but the sensitivity decreases as crude oil price increases.

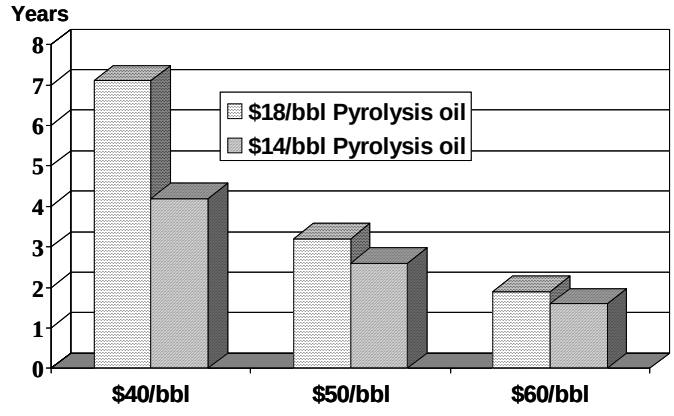


Figure 27. Years to payback for conversion of pyrolytic lignin to gasoline.

Table 29 shows the incentives for producing H_2 from the water-soluble portion of pyrolysis oil for $40/bbl crude and $10/bbl pyrolysis oil. Pyrolysis oil must be less than $12/bbl before there is a positive incentive for H_2 production. The incentive is $3.5MM/year with the CO_2 credit and $0.3MM/year without.

The capital cost of a pre-reformer to add to an existing H_2 plant is $15MM. Unless pyrolysis oil price drops, it is better for a refiner to simply co-fire the aqueous phase pyrolysis oil as fuel, replacing natural gas which is used in the refinery.

Table 29. Incentives for H_2 production

	$/D	Quantities
Feed		
Water-soluble pyrolysis oil	52,500	5.250 bpd
Products		
Hydrogen	84,910	28 MMSCFD
CO_2 credit ($30/ton)	9,770	
Utilities	-31,500	
Incentive	10,680	

Table 30 shows the economics of cofiring the water soluble portion of pyrolysis oil and making gasoline from the pyrolyic lignin. Figure 28 shows the time to payback for conversion of the pyrolytic lignin to gasoline and co-firing of the water soluble pryolysis oil as a fuel substitute for natural gas.

Table 30. Overall incentives for use of pyrolysis oil for fuel and gasoline production.

	$/D	Quantity
Feed		
Pyrolysis oil	135,000	7500 bpd
Water Soluble Pyrolysis Oil		5250 bpd
Pyrolytic Lignin		2250 bpd
Products		
Fuel	66174	5250 bpd
Lt Hydrocarbons	19,303	64 tpd
Gasoline	52,520	1010 bpd
Diesel	12,000	250 bpd
CO_2 credit ($30/ton)	19,060	
Utilities	- 4800	
Incentive	29257	

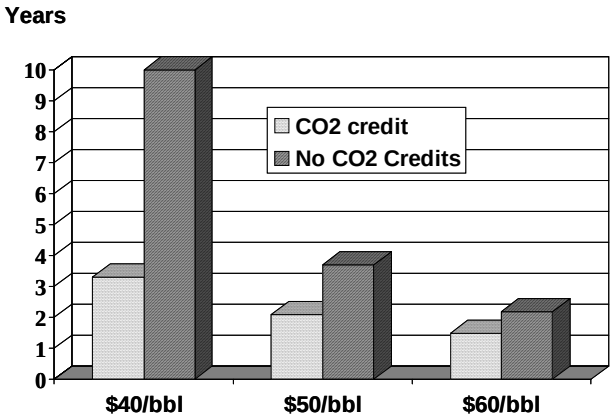


Figure 28. Years to payback for combined process.

V OPPORTUNITIES FOR FISCHER TROPSCH LIQUIDS

Another option for biorenewable use is gasification followed by Fischer-Tropsch (FT) synthesis from the syngas. The properties of crude FT liquids are summarized in Table 31 and Table 32. Crude FT liquids contain some oxygen and olefins which are easily removed by hydrotreating. The study calculated the value of FT liquid to a typical refiner if biorefineries chose to send them to the refinery rather than upgrade the FT themselves. The yields and properties are based on an iron fixed bed FT system marketed by Rentech.

Table 31 Properties of crude FT liquids

	Crude	Resid	Crude FT Liquids
% C	83-86	84.9	82.8
%H	11-14	10.6	14.0
%S	0-4 (1.8avg)	4.2	-
%N	0-1 (.1avg)	.3	-
%O	-	-	3.2
H/C	1.8-1.9	1.5	2.0
Density	.86(avg)	1.05	0.82
TAN #	<1	<1	Low
Heating value BTU/lb	18,000	17,500	18,400

Table 32. Detailed properties of crude FT liquids.

	Naphtha	Diesel	Wax
Wt%	19	21	60
Density	0.76	0.79	0.85
BP, F	70 – 320	320 – 650	650+
Wt% Oxygen	6	6	1.3
Wt% Saturates	22	30	88
Wt% Olefins	48	14	6
Wt% Alcohols	26	16	6

The configuration of a typical hydrocracking-based refinery was shown in Figure 5 of Section II.2.3. In order to maximize diesel production, the wax is cracked in a hydrocracker (HCK) to make diesel and the naphtha and diesel must be hydrotreated to remove oxygen and olefins.

There are a number of options possible for integration with a typical refinery. These include:

- Send FT Liquids to the crude tower if all diesel is hydrotreated. This places a penalty on gasoline produced (poor octane) but requires no capital.
- Send everything to the HCK. This results in yield loss from cracking diesel but requires no capital.
- Send FT liquids to their own tower, while sending the diesel and naphtha cut to DHT and the wax cut to HCK to produce diesel and naphtha. Capital is required for two towers and typical HCK conditions are not optimal for FT wax.
- Send FT liquids to their own tower, while sending the diesel and naphtha cut to DHT and the wax cut to low pressure HCK (converted DHT). Capital is required for two towers if DHT is available for use as HCK (optimal configuration).

Sending FT their own tower and processing the wax in the hydrocracker and the naphtha and diesel in the DHT is the best option, but does require a small investment in two distillation

towers. The resulting configuration is shown in Figure 29. The value of the FT liquids to the refiner is shown in Table 33.

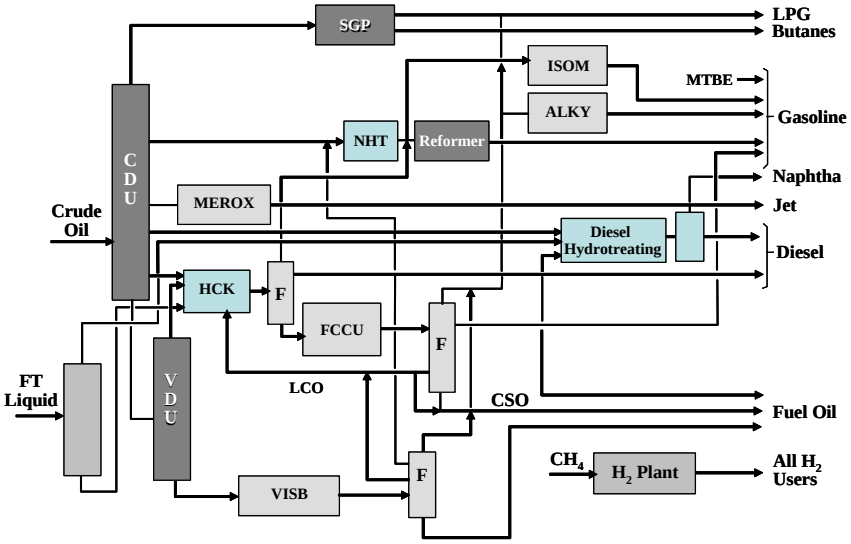


Figure 29. Typical hydrocracking refinery processing crude FT liquids.

Table 33. Value of crude FT liquids to refiners.

	Starting wt%	Wt% after conversion	Value $/ton	Total Value $/ton
Lt ends		3.7	320	11.8
Naphtha	19	28.9	324	93.6
Diesel	21	66.4	368	244.4
Wax	60			
Water		3.5		
H_2 use		-1.4	1200	-16.4
Operating cost and refinery margin				-20
Total value $/ton				**313**

VI ACRONYMS AND ABBREVIATIONS.

Table 34 lists the acronyms and abbreviations used elsewhere in this report.

Table 34. Acronyms and abbreviations.

Acronym or Abbreviation	Definition
ABT	Average bed temperature
APR	Aqueous phase reforming
bbl	Barrel(s)
bpd	Barrels per day
bpsd	Barrels per stream day
Br No	Bromine Number
COP	Cost of production
CSO	Clarified Slurry Oil
DeCO2	Decarboxylation
DHT	Distillate hydrotreater
EEC	Estimated erected cost
EOR	End of run
FAME	Fatty acid methyl esters
FCC	Fluid catalytic crackers
FFA	Free fatty acid(s)
FT	Fischer-Tropsch
GJ	Gigajoule = 1.055 MMBtu
HC	Hydrocarbon(s)
HCK	Hydrocracking
HDM	Hydrodemetallization
HDO	hydrodeoxygenation
HDS	Hydrodesulfurization
HP	High pressure
HT	Hydrothermal
HT	Hydrotreating
LCA	Life-cycle analysis
LCO	Light cycle oil
LHSV	Liquid hourly space velocity
LHV	Lower heating value
LPG	Liquified petroleum gas
lv%	Liquid volume %
MCFD	Million cubic feet per day
mf, m.f.	Moisture-free

MMBtu	Million Btu
MTBE	Methyl tertiary butyl ether
NPV	Net present value
POP	Proof of principle
POX	Partial oxidation
PRSV	Peng-Robinson-Stryjek-Vara
PSA	Pressure swing adsorption
scfb	Standard cubic feet per barrel
SMR	Steam methane reforming
SOR	Start of run
SS	Stainless steel
TAN	Total acid number
tpd	Tons per day
ULSD	Ultra-low sulfur diesel
VGO	Vacuum gas oil
VHP	Very high pressure
WHSV	Weight hourly space velocity
WTI	West Texas Intermediate

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OPPORTUNITIES FOR BIORENEWABLES IN OIL REFINERIES

APPENDIX:

BACKGROUND AND EXPERIMENT SUMMARY

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A select set of experiments performed in the project are summarized in Table 1 and Table 2.

Table 1. Experiment summary (Part I).

	524	529	531	535	537	538	540
Feed	vegetable oil			HT-82 (HT lignin)	Pyrolytic lignin (Dynamotive)		Pyrolysis Oil
Conditions							
Temperature	300-350	300-350	300-350	370	350	350	350
Time at temp hr	2.1	1.88	1.7	2	3	4	3
Catalyst	AS-250	HCT-1	N200	HC43	HCT	HCT	HCT
Cat amt ,g	25	25	25	25	25	25	25
Feed amt	75	75	75	75	75	150	75
WHSV	1.4	1.6	1.76	1.5	1	1.5	1
LHSV	0.91	1.40	1.26	0.96	0.67	1.01	0.67
Pressure psig	500	500	500	1500	1500	1500	1500
Products							
Water % of feed	2	1.7	1.15	7.5	24.1	23.8	33
Water from organic % of feed				4.6	12.4	12.1	6.3
Light liquids %	4.8	0.09	0.64	30	27.7	19.8	19
Diesel %	65.07	78.5	76.4	29.4	12.8	28.8	19.9
VGO % (necessary to remove to reach diesel spec)			3.2				
Total % liquid product	69.87	78.59	80.24	59.4	40.5	48.6	38.9
Gas and lights(by difference)	28.13	19.71	18.61	33.1	35.4	27.6	28.1
Calculated CO2+CO	10.9	12.7	13.4	18.4	24.0	18.6	37.1
Lt Hc and loss calc	17.3	7.0	5.2	14.7	11.4	9.0	-9.0
Total	100	100	100	100	100	100	100
% triglyceride conversion	100	100	100				
% O in liquid product	3.4	1.3	0.9	1.8	4.8	7.3	5.5
%O in naphtha				1.3	5.9	7.2	8.6
%Oxygen in diesel+	3.4	1.3	0.9	2.3	2.4	7.3	2.4
%Oxygen removal	81.2	90.1	91.3	94.5	94	90	96
% O to water	15	12.8	9.8	34.36	58.53	57.80	53.33
% Organic O to water				31.79	48.13	47.40	29.60
% oxgen to Co and Co2	66.2	77.3	81.5	60.14	41.47	32.20	42.67
% feed to CO2(calc)	10.9	12.7	13.4	18.4	24.0	18.6	37.1
%organic Oxygen to Co+Co2				62.7	45.9	42.6	66.4
%NC15	6	9	8.9				
%IC15	2		1.2				
%NC16	3	3	4.6				
%IC16	2	0.5	1.4				
%NC17	37	55	43.6				
%iC17	1.8	2	4.1				
%NC18	19.6	18.5	21.1				
%iC18	2	3.5	5.33				
Total	73.4	91.5	90.23				
Feed %Oxygen	10.4	10.4	10.4	19.4	36.6	36.6	57
Feed density	0.92	0.92	0.92	1.03	1.2	1.2	1.2
Acid number feed				34	168	168	75
Water in feed				2.9	11.7	11.7	26.7
Feed IBP				21			
Feed 10%				126.6			
Feed 30%				225.4			
Feed 50%				323			
Feed 70%				413			
Feed 90%				529			
Feed EP				607			

Table 2. Experiment summary (Part II).

	524	529	531	535	537	538	540
Feed		vegetable oil		HT-82 (HT lignin)	Pyrolytic lignin (Dynamotive)		Pyrolysis Oil
Acid number product							
Acid number trap HC					15.1	24.11	43
Acid number diesel						0	
Naphtha density				0.81			
Diesel density							
Distillations							
Product IBP C				-8			
Product wt 10%				105			
Product 30%				157			
Product 50%				199.5			
Product 70%				246.5			
Product 90%				332			
Product EP				592			
%m TOC in water					2.4	4.1	3.2
naphtha fischer water				946ppm			
Naphtha IBPC				-8	20	-10	25
10%				71	80	22	86
30%				105	133	105	147
50%				143	173	109	195
70%				181	216	138	243
90%				226	277	201	310
EP				321	459	312	422
Naptha %C				86.1	82.7	78.4	78.6
Naptha %H				12.6	11.4	10.1	11
Naphtha %O by dif				1.3	5.9	11.5	10.4
Diesel_ IBP				50	24		
10%				139	267		
30%				209	319		
50%				256	358		
70%				312	413		
90%				438	500		
EP				592	600		
Diesel %C	82.8	84.5	84.7	87.1	87.2	83.9	87.6
Diesel %H	13.7	14.2	14.4	10.3	10.4	8.8	10
Diesel %O(by dif)	3.5	1.3	0.9	2.6	1	7.3	2.4
Comment	- Lots of cracking - No gas samples - Some isom.	- Less cracking - Some gas samples - Less isom.	Too much heavy ends				some coking

We provide here supporting information for the study basis outlined in Section II.2 of the report.

Table 3 lists some of the significant U.S. and international mandates that will drive increased use of biofuels in the next few years.

Table 3. Global mandates for biofuel usage.

	2005	2010	Type	2010 Targets (bbl/d)
EU	2% biofuels	5.8% biofuels	Law	200,000
U.S. diesel	No % but high subsidies for biodiesel	2.5%	Goal	100,000
U.S. ethanol	2.2% of gasoline	3.5% of gasoline	Goal + Law	325,000
India		5-10%	Goal	80,000-160,000

Table 4 lists the base prices of feeds used in the study. Bio-feedstock prices were based upon an average of 2003 – 2004 values reported in the Chemical Marketing reporter.

Table 4. Base prices.

	$/unit	$/ton
WTI Crude	40/bbl	306
Arab Medium	36.5/bbl	237
Reg Gasoline	49/bbl	410
Premium gasoline	52/bbl	435
Diesel	48/bbl	343
Residual Oil	27/bbl	173
Methanol	34/bbl	275
Soy Oil without subsidy	0.25/lb ($73/bbl)	559
Soy Oil with subsidy	0.06/lb ($17/bbl)	132
Yellow Grease without subsidy	0.14/lb ($41/bbl)	310
Yellow grease with subsidy	0.02/lb ($6/bbl)	44
Brown Grease	0.06/lb ($18/bbl)	132
Pyrolysis Oil	16/bbl	83
Glycerol	0.10/lb	220
Methane(Natural Gas)	6.0/MMBTU	286
Toluene	62/bbl	450
Ethylene		695
Propylene		670
Propane	31/bbl	352
H2	3.1/MSCF	1200
Benzene		700
Xylene		575
Crude tall oil		100

Subsidies were calculated based on the subsidies for biodiesel shown in Table 5.[1]

Table 5. Biodiesel subsidies (feedstock prices from crop year 2003/04 projections).

Feedstock	Feedstock Price,$/lb	Total Production Cost, $/gal B100 *no incentives*	EstimatedCCC Incentive	Net Biodiesel Production Cost, $/gal B100	Net Biodiesel $/gal B20 *with tax credit*
Soy	0.238	2.29	1.43	0.86	0.66
Sunflower	0.262	2.49	1.57	0.91	0.71
Corn	0.263	2.49	1.58	0.92	0.72
Peanut	0.436	3.9	2.62	1.28	1.08
Cottonseed	0.279	2.62	1.67	0.95	0.75
Safflower	0.735	6.32	4.41	1.91	1.71
Edible Tallow	0.164	1.69	0.98	0.71	0.61
Inedible tallow	0.151	1.59	0.91	0.68	0.58
Lard	0.179	1.81	1.07	0.74	0.64
Choice white grease	0.129	1.41	0.77	0.64	0.54
Yellow grease	0.104	1.21	0.62	0.58	0.48

[1] NREL. Presentation on Biodiesel Costs. July, 2003.

Table 6 and Table 7 list the costs of pyrolysis oil and related assumptions.

Table 6. Pyrolysis oil costs.

Biomass Federate	Biomass Feed Cost	Pyrolysis Oil Produced			Pyrolysis Oil Cost		
Tonne/day	$/dry ton	t/day	bbl/day	$/GJ (LHV)	$/MMBtu	$/BBL	$/BBL of FOE
500	$30.00	325	1705	$6.77	$6.42	$21.10	$51.79
500	$46.00	325	1705	$8.20	$7.77	$25.53	$62.67
2000	$30.00	1300	6820	$5.10	$4.84	$15.89	$39.01
2000	$46.00	1300	6820	$6.52	$6.18	$20.32	$49.88

Table 7. Additional assumptions.

1 GJ	1.055	MMBtu
1 Barrel	42	gallons
Density of Pyrolysis Oil	4.55	kg/gal
LHV of Pyrolysis Oil	16,300	kJ/kg
LHV of fuel oil (No. 6 Fuel Oil from Phyllis)	40,009	kJ/kg

The properties of typical biofeedstocks are summarized in Table 8. The low heating value for pyrolysis oil is the result of the high oxygen content. The high alkali metals in vegetable oil, grease and pyrolysis oil are mostly potassium and calcium.

Table 8- Feedstock properties

	Crude	Resid	Pyrolysis Oil	Soy Oil	Yellow Grease
% C	83-86	84.9	56.2	77/6	76.4
%H	11-14	10.6	6.6	11.7	11.6
%S	0-4 (1.8avg)	4.2	-	0.0006	0.04
%N	0-1 (0.1avg)	.3	0.3	0.0011	0.03
%O	-	-	36.9	10.4	12.1
H/C	1.8-1.9	1.5	1.4	1.8	1.8
Density	.86(avg)	1.05	1.23	0.92	0.89
TAN #	<1	<1	78	2	30
Ppm alkali metals	60	6	100	100	100
Heating value BTU/lb	18,000	17,500	6,560	16,000	16,000

The relative locations of Biofeedstock sources and refineries in the U.S are shown in Figures 1 and 2.

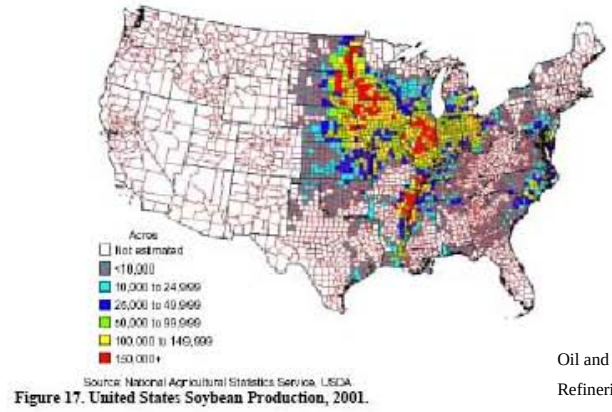


Figure 1. Locations of U.S oil, grease and refineries.



Figure 2. Locations of U.S. biomass and refineries.