Opportunities for Biorenewables in Petroleum Refineries

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Abstract

Biofuel production is expanding worldwide because of increasing petroleum prices; government mandates and incentives; and commitments to greenhouse gas (GHG) reduction. Despite this growth in biofuel production there is so far little integration of biofuels production within petroleum refineries. The segregation of biofuel production increases their cost since existing infrastructure for distribution and production of fuels is not utilized. Biofuels could more quickly alleviate a significant amount of the increasing demand for petroleum if economical opportunities for blending or co-processing them in traditional petroleum refineries could be identified and developed. Recently, a US Department of Energy funded collaboration between UOP, the National Renewable Energy Laboratory, and the Pacific Northwest National Laboratory completed an evaluation of the economics of biofuels integration in petroleum refineries. The purpose of this project was to identify economically attractive opportunities for biofuels production and blending using petroleum refinery processes. Economic analyses were conducted to assess a variety of potential processes and configurations using process modeling and proof of principle experiments. The main focus of the study was the production of fuel, power, chemicals and hydrogen from two broad feedstocks: vegetable oil and pyrolysis oil. The impact of biofuels integration on refinery GHG emissions was also examined. Many promising opportunities were identified for integrating biorenewable feeds and products in existing or new refining operations.

1. Introduction

The production of biofuels is expanding worldwide at a rapid pace due to factors cited above. The future widespread use of biofuels depends on solving several issues such as:

- Identifying a large, consistent quantity of renewable feedstock
- Producing biofuels at costs competitive with other fuels
- Transporting the biobased feedstock or fuel to distribution centers
- Developing new technology to produce fuels from the unique composition of these highly oxygenated feedstocks
- Producing biofuel compatible with the existing transportation and fuel infrastructure

The goal of this study was to identify profitable processing options for integrating biorenewable feeds and fuels into existing refineries by addressing these issues. Many options were identified including the production of liquid transport fuels through co-processing and modular production plants. Processes to convert these feedstocks into chemicals, hydrogen, and to produce power were also considered. Details of promising processing options were defined and followed with performance estimates. This procedure usually required proof of principle experiments in batch and continuous pilot plants with online analysis of products to provide data for models and correlations to estimate commercial performance. From these estimates the potential business value of biorenewable integration was evaluated and several variables were found to significantly affect the capital cost and net present value (NPV) of the various processing approaches, such as:

- A stand-alone process vs. co-processing
- The availability of government subsidies
- Crude oil prices

Government subsidies were required to make some of the processes economically attractive but several of the options were favorable without subsidies. All options become more attractive with high crude oil prices.

Although high oil prices make many of these options economical the processes identified in this study varied in the amount of commercial development required to produce biofuel. A schematic showing several options for biofuel production from different biomass sources in shown in Figure 1. Some of the routes are already in commercial practice, such as ethanol from the fermentation of corn or sugar cane. Others can be developed in the near term such as the deoxygenation of plant oils to produce a “green” diesel fuel. Several routes have a considerable longer timeframe for commercialization due to technical challenges or feedstock availability. Many of these processing routes for producing biofuel from vegetable oil and pyrolysis oil are discussed in this paper.

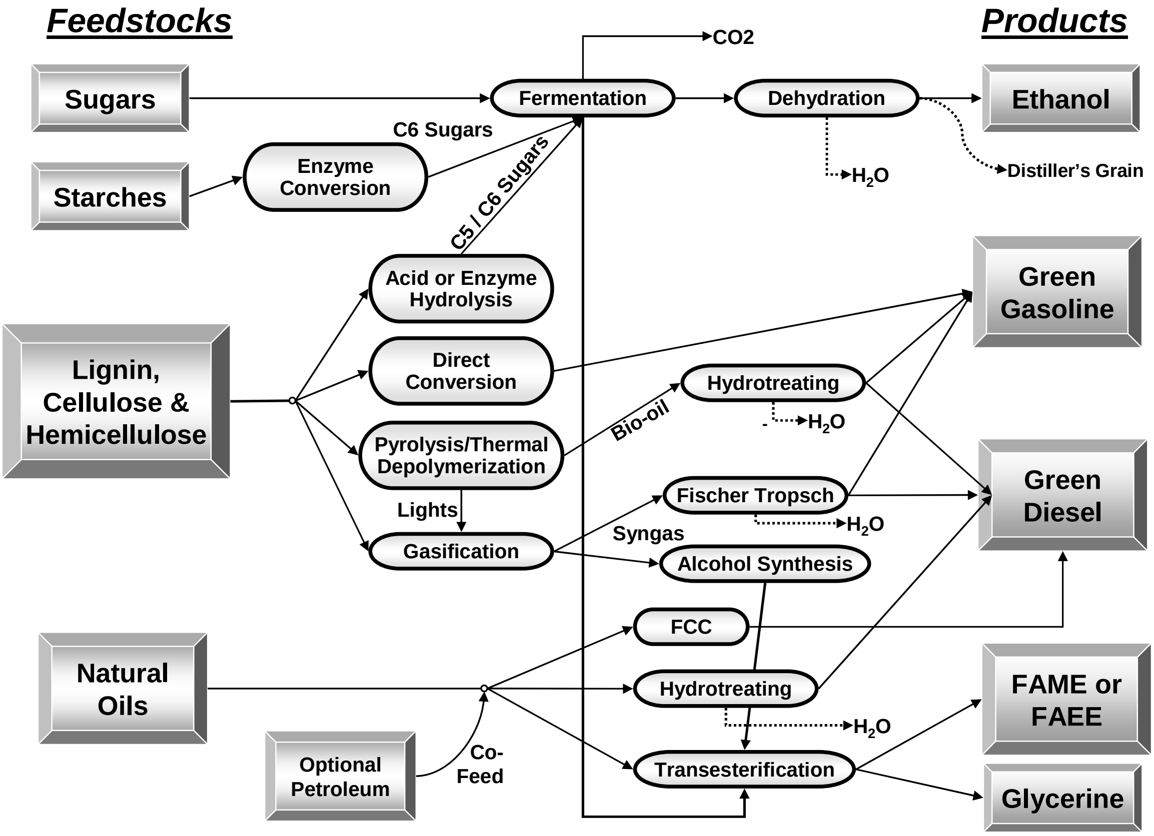

Figure 1. Overview of Biofuel Production

2. Study Basis and Methodology

The first question addressed was the availability of biorenewable feedstocks at 2005 levels. Table 1 shows the U.S. availability of several biofeedstocks while Figure 2 compares the global volume of petroleum-based liquid transport fuels with available vegetable oil and greases in 2005. For example, vegetable oils and greases could only replace a very small fraction of transport fuel. However, the potential large supply of lignocellulosic biomass could supply a high percentage of future liquid transport fuels if commercial processes were available to convert these feeds. One such process evaluated in this study was fast pyrolysis but the quantity of pyrolysis oil is currently very low since commercial production is still at an early stage.

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

Biorenewable Feedstock	Definition	Amount produced in the U.S. (bpd)	Amount available for fuel production in U.S. (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	Made from pyrolysis of waste biomass (cellulosic)	1,500	750

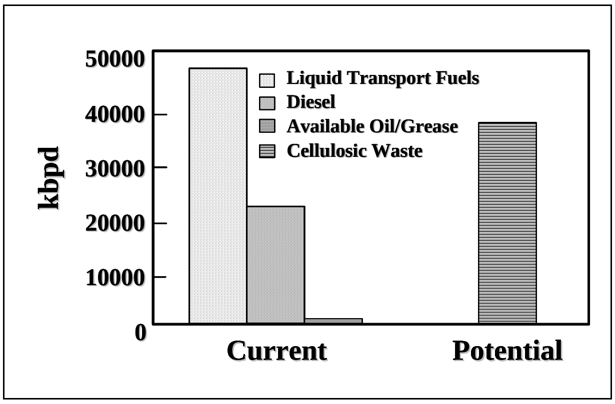

Figure 2. Availability of biorenewable feedstocks in the U.S[6,7]

The study took into account both feedstock costs and the projected prices of potential products. Prices of raw vegetable oils, greases, and pyrolysis oils were determined and used in the economic assessment. The costs ranged from $16/bbl for pyrolysis oil to $>75/bbl for raw vegetable oils. Each economic analysis was primarily based on a West Texas Intermediate (WTI) crude feedstock price of $40 per barrel, a level considerably lower than the recent >$60/bbl price. The cost of each potential biofuel was compared to this crude feedstock price after incorporating a number of factors including capital costs; transportation costs; CO_2 credits; subsidies; and cetane and octane numbers.

Most of the feedstocks looked promising when current subsidies were applied and several were economically attractive without subsidies such as pyrolysis oil and brown grease. Raw vegetable oils were not attractive without subsidies until crude prices are > $70/bbl.

The properties of biorenewable feedstocks were compared to petroleum as shown in Table 2. The biggest difference between biorenewable and petroleum feedstocks is oxygen content. Biorenewables have oxygen levels from 10-40% while petroleum has essentially none making the chemical properties of biorenewables very different from petroleum. For example, these feedstocks are often more polar and some easily entrain water and can therefore be acidic. All have very low sulfur levels and many have low nitrogen levels depending on their amino acid content during processing. Several properties are incompatible with typical refinery operations such as the acidity and alkali content so that processes were identified to pretreat many of these feeds before entering refinery operations.

Table 2. Typical Properties of Petroleum and Biorenewable Feedstocks

	Petroleum		Biorenewable		
	Crude Typical	Resid	Soyoil	Yellow Grease	Pyrolysis Oil
% C	83-86	84.9	77.6	76.4	56.2
%H	11-14	10.6	11.7	11.6	6.6
%S	0-4 (1.8avg)	4.2	.0006	.04	-
%N	0-1 (.1avg)	.3	.0011	.03	.3
%O	-	-	10.4	12.1	36.9
H/C	1.8-1.9	1.5	1.8	1.8	1.4
Density	.86(avg)	1.05	.92	.89	1.23
TAN	<1	<1	2	30	78
ppm alkali metals	60	6	100	100	100
Heating value kJ/kg	41,800	40,700	37,200	37,200	15,200

3. Refining Opportunities for Vegetable Oils and Greases

A large number of options were identified for processing vegetable oils and greases in refineries as shown in Figure 3. One is catalytic cracking to produce either green gasoline or green olefins, depending on the process conditions and catalysts, to produce fuel or valuable chemicals such as ethylene and propylene. Likewise, these oils could be deoxygenated using existing hydroprocessing technology to produce a high-cetane green diesel product. Different fits for the production of biodiesel in refineries were also evaluated but are not discussed in this paper.

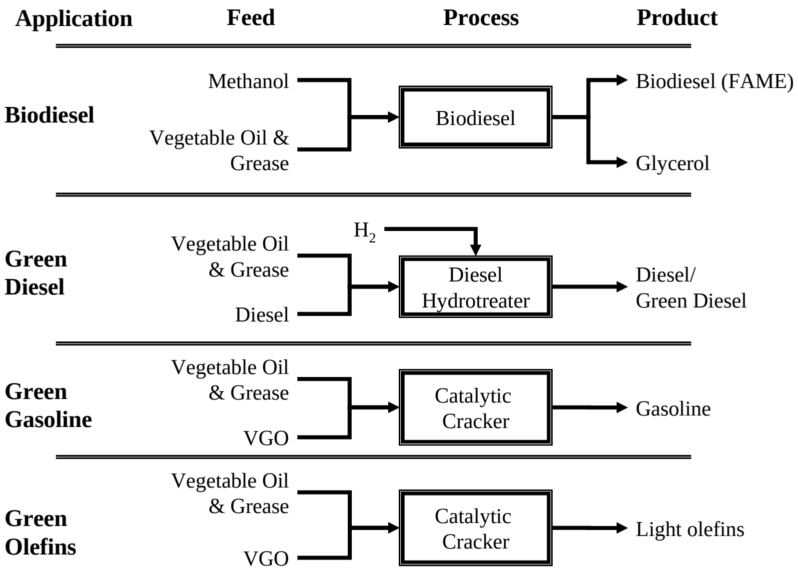

Figure 3. Processing routes for vegetable oils and grease

3.1. Catalytic Cracking of Vegetable Oils and Greases

Processing options for the catalytic cracking of vegetable oils and greases were identified and one example is shown in Figure 4, where a pretreatment unit is required to remove catalytic poisons such as alkali metals and other problematic components such as water and solids. The pretreated feed can then be coprocessed with crude to produce gasoline and other products. Furthermore, a modified catalytic cracking process can produce high value products such as ethylene and propylene.

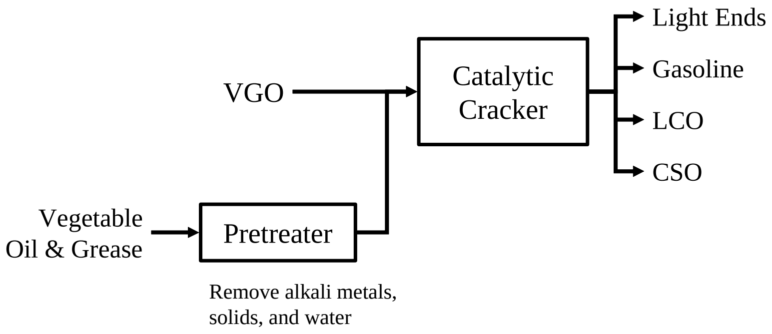

Figure 4. Processing approach for catalytic cracking of vegetable oil and grease

Estimates for each processing option are shown in Tables 3 and 4. Vegetable oil and greases produce gasoline yields very competitive with petroleum crude with reduced yields of heavier and often undesirable products such as LCO and CSO. Such processing also produces a significant amount of water and/or CO_x as a consequence of feedstock deoxygenation. Results were similar for olefins production where vegetable oil and greases can produce competitive yields of ethylene and propylene with reduced amounts of gasoline, LCO, and CSO. RON values are slightly higher for processing vegetable oils in both catalytic cracking schemes while coke yields are slightly higher for gasoline production. In either case the use of vegetable oils and greases in catalytic cracking units is feasible and attractive.

Table 3. Estimated green gasoline yields

	VGO	Vegetable Oil/Grease
C_2=	1.5	1.9
C_3P	0.7	0.8
C_3=	4.0	4.5
C_4s	7.9	6.5
Gasoline	45.5	44.9
LCO	17.5	11.3
CSO	19.5	12.7
Coke	3.4	4.5
Water/CO_X (Est.)	0	12.7
RON of Gasoline	92.1	94.8

Table 4. Estimated green olefins yields

	VGO	Vegetable Oil/Grease
C_2P+Methane	4.1	4.0
C_2=	8.6	8.6
C_3P	2.0	2.0
C_3=	22.0	22.2
C_4s	15.0	13.4
Gasoline	27.3	22.7
LCO	9.5	4.9
CSO	5.0	3.0
Coke	6.5	6.5
Water/CO_X (Est.)	0	12.7
RON of Gasoline	94.8	96.8

3.2. Hydroprocessing Vegetable Oils and Greases to Produce Green Diesel

The use of existing hydroprocessing technology was evaluated for the deoxygenation of vegetable oils and greases to produce a paraffinic diesel fuel through two promising processing options. As with catalytic cracking, co-processing in existing units requires a pretreatment unit to remove alkali metals and hydrogenate units of unsaturation on the fatty acid chains. The pretreated feed is then fed to an existing hydrotreater to produce a high cetane diesel product. An alternative is to produce the green diesel in a separate modular unit where processing conditions are optimized for the vegetable-oil-based feedstock. This modular unit could be constructed at an existing refinery or at remote locations. The paraffinic product could be blended with the hydrotreated diesel or could serve as a high quality diesel fuel on its own. This latter approach is attractive for feedstocks containing high percentages of free fatty acids or when transportation of the feedstock is prohibitively high since construction near the feedstock source and the choice of proper metallurgy will solve both issues.

Performance estimates for a green diesel process are shown in Table 5. Hydrogen requirements are variable depending on both the degrees of unsaturation on the fatty acid chains and the deoxygenation mechanism which itself depends on the choice of catalyst and processing conditions. Hydrodeoxygenation produces water and requires one hydrogen molecule for each oxygen removed while decarboxylation removes one carbon to produce CO or CO_2. Breaking the triglyceride backbone produces propane or lighter hydrocarbons. The yield of a high cetane and low sulfur-content green diesel product is >98% on a volumetric basis.

Green diesel is a fully-deoxygenated paraffinic feed and has several advantages over biodiesel, also produced from vegetable oil, as shown in Table 6. It is produced as a high-cetane, straight-chain paraffin but its cold-flow properties can be adjusted by the appropriate level of isomerization. The product cetane number can reach as high as 80-90. Biodiesel, a fatty acid methyl ester (FAME), contains a significant amount of oxygen that lowers its heating value and contributes to higher NOx emissions for concentrated blends. There are some other differences in product properties not identified in the table. The production of FAME yields a significant amount of contaminated glycerol byproduct that needs a commercial outlet while green diesel produces light hydrocarbons from the triglyceride backbone. The production of biodiesel requires a less flexible range of vegetable oil feedstock and fatty acids must be removed prior to transesterification. Highly unsaturated fatty acids chains result in a less stable biodiesel product since oxidation occurs at the double bonds when stored for extended periods of time. Green diesel has several property advantages over biodiesel and will likely be preferred by vehicle manufacturers.

Table 5. Performance Estimates for Green Diesel Process

Products	
Vol % Naphtha	< 1%
Vol % Diesel	>98%
Cetane Number	80-100
ppm S	<10

Table 6. Comparison of 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

3.3. Economic Analyses of Vegetable Oil and Grease Processing

Economic comparisons for the various processing options for vegetable oil and greases are shown in Figure 5 and Figure 6. First, a comparison of estimated capital costs is shown in Figure 5. 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. The EEC has an anticipated accuracy of -30%/+50%. The table shows that producing biodiesel has higher capital costs since it requires a more complex processing plant.

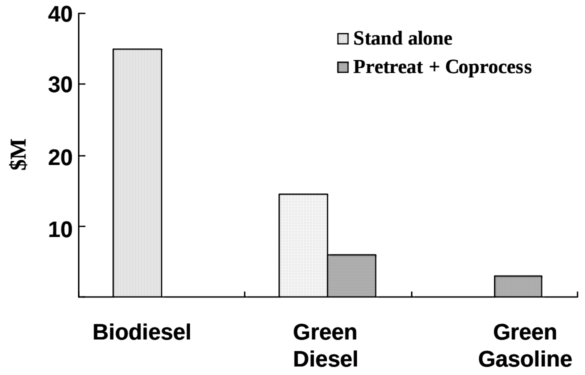

Figure 5. Capital costs of biofuels production from oils and greases.

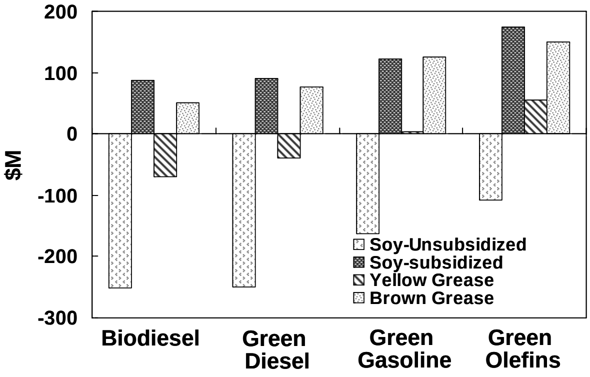

Figure 6. NPV comparison of biofuels and chemicals[8,9,10,11]

Figure 6 summarizes the economic analyses of biofuels and chemicals production from oils and greases comparing the NPV's of four products as a function of feedstock. Biodiesel is the least cost-competitive product for any feedstock, due to the high capital cost of biodiesel production. The effects of potential subsidies on NPV are included and 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 processing soy-based products.

4. Refining Opportunities for Pyrolysis Oil

Fast pyrolysis is a thermochemical process with the potential to convert the large volumes of cellulosic biomass available in the U.S. and globally into liquid fuels and feeds. A solid biomass feedstock is injected into a fluidized bed with high heat transfer capability for short contact times followed by quenching to condense a liquid biooil in 50-75% yields with gas and char forming the balance. The biooil contains the thermally cracked products of the original cellulose, hemicellulose, and lignin fractions present in the biomass. It also contains a high percentage of water, often as high as 30%. The total oil is often homogeneous after quenching but can easily be separated into two fractions, a water soluble fraction and a heavier pyrolytic lignin fraction. The addition of more water allows the pyrolytic lignin fraction to be isolated and the majority of it consists of the same phenolic polymer as lignin but with smaller molecular weight fragments. Pyrolytic lignin is a better feedstock for liquid fuel production than the water-soluble fraction because of its lower oxygen content and therefore the study focused on evaluating it as a potential feedstock for the production of highly aromatic gasoline. Commercial outlets for the water-soluble oil were identified and evaluated, such as the production of hydrogen and as a fuel for power generation. These latter applications will not be discussed here.

Table 7 shows an estimated performance for hydroprocessing pyrolytic lignin to produce biofuels based on experimental results. These estimates were used as a basis for economic calculations. The naphtha and diesel are produced along with a large amount of water and CO_2 due to water removal and deoxygenation. As with the vegetable oil the consumption of hydrogen and yield of CO/CO_2 will vary depending on the mechanism of deoxygenation.

Table 7. Performance estimates for the production of naphtha and diesel from pyrolysis oil

Feed	Wt%	bpd
Pyrolytic Lignin	100	2,250
H2	4-5	
Products		
Lt ends	15	
Naphtha	30	1,010
Diesel	8	250
Water, CO2	51-52	

The economics for producing fuels from pyrolytic lignin are shown in Table 8, assuming $18/bbl pyrolysis oil ($16/bbl +$2/bbl transportation charges) and two crude oil prices: $40 & $50/bbl.

Table 8. Performance estimates for the production of gasoline and diesel from pyrolysis oil

			$40/bbl Crude	**$50/bbl Crude**
		bpd	$/D	$/D
Feed	Pyrolytic Lignin	2,250	40,500	40,500
	H2	21.4 T	25,680	25,680
Products	Lt Hydrocarbons	64T/D	19,303	23,164
	Naphtha	1,010	52,520	62,510
	Diesel	250	12,000	15,000
Other	Utilities		-4,800	-5,760
	Net		12,843	28,734
	Annual Value		$4.2MM	$9.5MM

The value of producing liquid transportation fuels from pyrolysis oil is sensitive to both the price of the crude and feedstock. The sensitivity to feedstock price decreases with increasing crude oil price as shown in Figure 7 where the years required for payback of the capital investment is shown for several different prices of crude and pyrolysis oils. This figure is based on a capital cost of $30 MM for a hydrotreating/hydrocracking unit producing 1,010 bpd of gasoline. Producing fuel becomes economically attractive for $18/bbl pyrolysis oil at a crude price of $50/bbl. As pyrolysis oil price decreases, producing fuels from pyrolytic lignin becomes attractive at lower crude oil prices.

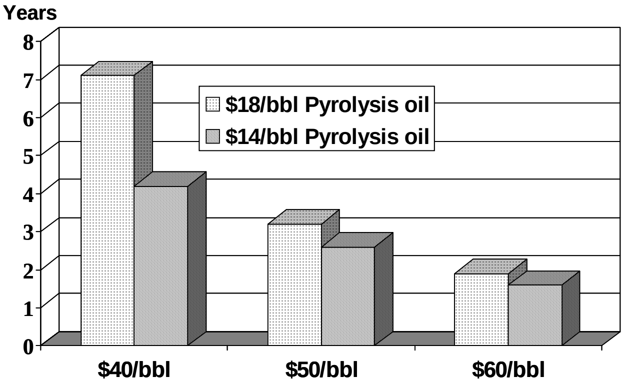

Figure 7. Years to payback for conversion of pyrolytic lignin to gasoline.

5. Life Cycle Analysis of Vegetable Oil Processing Options

A life-cycle analysis (LCA) of the various vegetable oil processing routes was conducted at Michigan Technological University using the Simapro^{TM} 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. 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 8. In general, the green products have much lower total environmental impact scores than petroleum diesel primarily because of significantly lower production of climate-active CO_2. Of the biofuels, green diesel and green gasoline (from catalytic cracking of vegetable oil) have the lowest environmental impact and CO_2 production. The environmental impact of biodiesel production is higher due to the methanol requirement which is produced from natural gas through an energy-intensive process with a strong environmental burden.

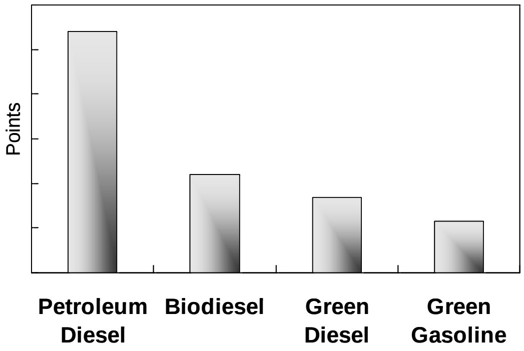

Figure 8. LCA – single environmental impact score.

5. Summary

Many economically attractive opportunities were identified in this study for the integration of biorenewable feedstocks and biofuels in petroleum refineries, particularly for two promising feedstocks:

- Vegetable oils/greases to produce green diesel, gasoline, or chemicals
- Pyrolysis oil to produce green gasoline

Vegetable oil can be processed in the short term using commercially available refining technology but will be limited to producing a small fraction of liquid transport fuels due to a limited amount of feedstock. Pyrolysis oil processing requires more commercial development and is also limited by the availability of pyrolysis oil since commercial production is still in its infancy. In the long term, however, the potential volume of pyrolysis oil could replace shortages in petroleum fuel since it can process the large amount of cellulosic biomass available.

Acknowledgements

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