Integrated Multistage Supercritical Technology to Produce High Quality Vegetable Oils and Biofuels

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ABSTRACT

A multi-step integrated technology to produce vegetable oils and biodiesel (BD) is proposed, documented for technical and economic feasibility, and preliminarily designed. The 1st step consists of soybean oil extraction with supercritical (SC) fluids. The 2nd step is designated to transform the soybean oil into BD by transesterification (TE) with SC methanol/ethanol. The degradation of glycerol to light fuel products makes this method simple and cost effective by eliminating costly glycerol separation steps. Part of the BD is in-situ consumed by a diesel engine which, in turn, provides the mechanical power to pressurize the system as well as the heat of the exhaust gases for the extraction and TE steps. Different versions of this system can be implemented based on the main target: oil and BD production or diesel engine applications. The efficiency of the combustion and cleaner emissions render the proposed technology attractive for the transportation sector with only TE step needed to provide fuels to engines.

Keywords: integrated supercritical technology, supercritical extraction of soybean oil, supercritical transesterification, biodiesel, economic analysis.

1   INTRODUCTION

Unfortunate developments in crude oil prices combined with disruptions in supply and refining capacity have given new urgency to the development of alternative, renewable fuels that not only reduce the reliance on petroleum feedstock, but also result in reduced emissions of airborne pollutants. Biodiesel (BD) derived from plant/animal fats is one such fuel that is under a great deal of consideration.

We propose to produce BD with a continuous integrated process, starting with soybean oil (SO) extraction in multiple extractors and cascaded separators. The extraction step should use three parallel batch extractors with supercritical (SC) carbon dioxide (CO_2), and CO_2 recovery stages. The BD production step will use the extracted oil or oil from other sources and SC methanol/ethanol in a continuous tubular reactor without catalysts and multi-step separations. The process will use a diesel generator to provide power and heat for the upstream processes.

If implemented, this integrated system has potentially a wide range of applications. First, it is very attractive for farmers by reducing their dependency of high petroleum fuel prices. Many farmers which crop soybeans already use

SO as a fuel. However, SO is not an acceptable fuel because of the damage it renders to the engines, especially on long-term usage. Secondly, this system, without the SC extraction (SCE) step, should have great potential to be implemented on transportation vehicles since only a small reactor is required to be inserted between the injection pumps and common rails of diesel engines. All the needs for the TE reaction to proceed are already available with these engines, including the free heat of the exhaust gases.

The overall goal of this study is to develop an industrial technology for continuous SO extraction coupled to BD production by using a SC alcohol as shown in Figure 1. Specific objectives for this stage of the project were to: (i) develop a conceptual design with key steps established for the integrated process, (ii) determine optimal parameters for oil extraction and the reaction parameters and yields at lab-scale, and (iii) perform an economic analysis for easy comparison with current methods.
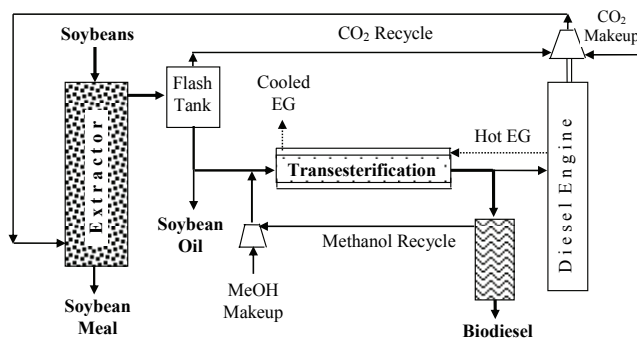

Figure 1: *Integrated Multistage SC Technology System* to produce vegetable oils and biodiesel (schematic).

2   CONCEPTUAL DESIGN

2.1   Supercritical Oil Extraction

For the *extraction step*, the reported data corroborated with our own experimental information show that SCE of SO requires high pressures (beyond 400 bar, with our results suggesting the lower limit of these ranges) and relatively high temperatures (>80°C, with our optimum yield at ~100°C) for acceptable high efficiencies of oil recovery when pure SC CO_2 is used. However, under either of these conditions, appropriate process optimization can render this method competitive with the conventional

extraction with liquid hexane [1]. Also, we expect that a further suitable selection of a co-solvent such as propane/butane can lower the extraction conditions of *P-T* parameters with significant cost savings. Alcohols and pentanes/hexanes should be excluded due to their interaction and extraction of the proteins. Furthermore, a battery of three coupled extractors makes this step quasi continuous with positive results on cost cuttings.

2.2 Oil Transesterification

In the *transesterification step*, BD is prepared from SO and SC methanol/ethanol. The conditions at which bulk glycerol decomposed in our reaction system have been determined as 350-400°C and 100-300 bar. Here we assume that the reaction is pseudo first order and the reverse reactions are not significant. These assumptions were made as for the design proposed we are using a stoichiometric alcohol to oil molar ratio of 3:1. We will also carry out experiments to explore and gather more information about the aforesaid issues and refine, reevaluate, and reassess our design. However, when a TE process in an industrial scale flow reactor will be implemented, a possible separation of glycerol and BD phases will be less complicated than the acid/base catalyzed TE process.

In conclusion, a conceptual design for the integrated steps of extraction and TE, including a diesel engine as a source of energy, is schematically shown in Figure 1. Updated modifications will be implemented as research progresses in the next stages of this project.

3 EXPERIMENTAL RESULTS

Using a high pressure view cell as a diagnostic aid, it was found that the oil miscibility with methanol is crucial to attaining a high conversion to BDF. Experiments have been carried out with this apparatus to test its capabilities regarding SO-MeOH miscibility and phase transitions under different *P-T-composition* conditions. The results for equal volumes of SO and MeOH heated in the view cell in a batch mode are shown in Figure 2. In this case, SO and methanol are only partially miscible from room *P-T* conditions up to near 400°C, while beyond 400°C and 100 bar, one homogeneous phase has been obtained. These experiments are very important because complete TE reactions can be achieved, in a reasonable short time, only under complete miscibility conditions.

Figure 2 shows selected photographs of phase transitions associated with TE reactions between SO and methanol (3 mL each) heated from ambient T-P conditions to 420°C and 120 bar. The images (seen down the columns) are for SO(L)-MeOH(L) (#1), SO(L)-MeOH(L)-MeOH(V) (#2-3), SO-BDF-MeOH(L-SC) (#4-5), and BDF-MeOH(SC) (#6).

Figure 3 is a GC-MS comparison between commercial BD and our TE products which shows similar compositions with the latter containing fewer high molecular byproducts.
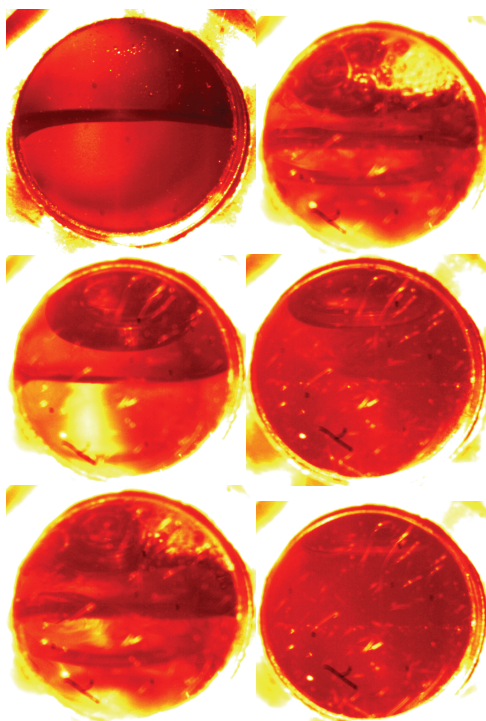

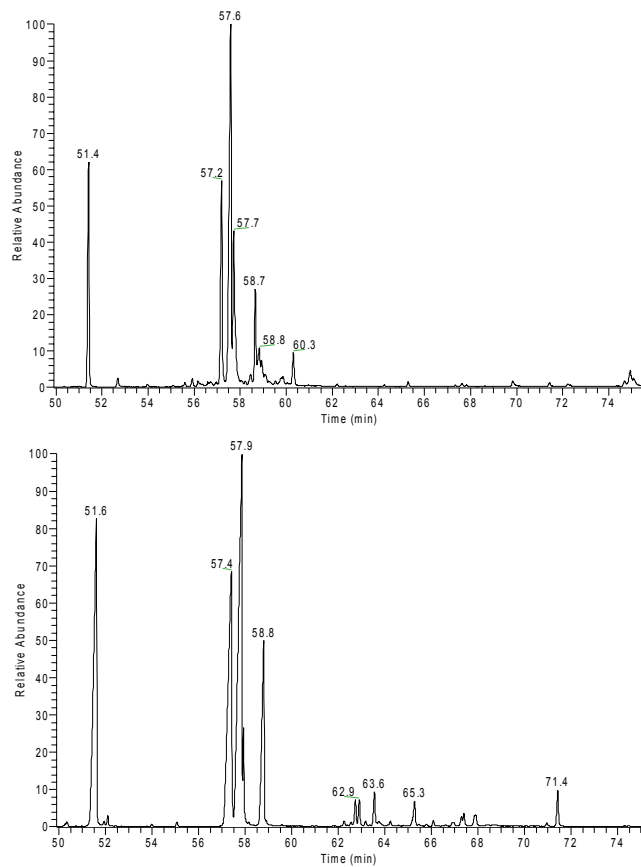Figure 2: Photographs of SO-MeOH phase transitions with TE reactions.

Figure 3: A GC-MS comparison between commercial BD (bottom) and TE products from our experiments (top).

4 ECONOMIC ANALYSIS

Economic estimates for different system configurations were performed to select the most desirable option based on maximum benefits.

4.1 Biodiesel Production

Experiments carried out in our laboratory have shown that reacting stoichiometric quantities of methanol or ethanol with SO at 400°C, 100 bar for about three minutes gives nearly complete conversion of the SO to BD (esterified fatty acids). Under these conditions, in contrast to the BD production under traditional conditions (1 bar, 65 °C, catalysts), the reaction rate is 60 times faster and very little glycerol is left in the final reaction products. Instead, other compounds are formed resulting from the breakdown of the glycerol. Not all of these products have been qualitatively and quantitatively determined, but it is expected that many of them can be used directly as part of the BD product. This would simplify the separation process greatly and additional BD fuel may be produced. In addition, under near stoichiometric SO:MeOH ratio, essentially all of the alcohol quantities will be consumed, eliminating the need for alcohol separation and recycling.

Thus, the process for producing BD from SO becomes quite simple: a reactor with a heat source to produce BD and one or two distillation columns to separate water and other impurities from the product. In our preliminary process design, the reaction product stream is assumed to contain only two glycerol degradation products, diglycerol and glycerol formal. These two products have been identified by GC/MS analysis of the product stream from the laboratory reactor. The process flow diagram is shown in Figure 4.
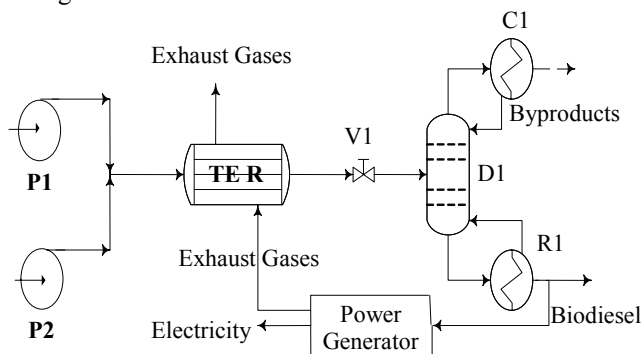

Figure 4: Process flow diagram for biodiesel production coupled with power generation. (P1, P2: oil and MeOH pumps; TE-R: transesterification reactor in a heat exchanger; V1: pressure reduction valve; D-1: distillation column; C1: Condenser; R1: Reboiler).

The process consists of pumping the methanol and SO to the TE reactor at 100 bar (the reactor operating at 400°C) and a distillation columns operating at 1 bar with steam driven reboilers and condensers cooled by cooling water. The distillation column separates the water and most of the reaction byproducts from the methyl esters. A 2nd column can be added, as needed, to separate byproducts from the water. The process is unique in that the exhaust gases from a diesel engine are used to provide heat for the reaction.

The basis for the base-case design was the TE of 2100 gal/day of SO with 269 gal/day of methanol to produce 2300 gal/day of BD. The plant was assumed to operate 24 hours/day for 346 days a year. The thermodynamic properties of SO, the methyl esters of the three main fatty acid chains of SO (palmitic, linoleic, and oleic) and the assumed byproducts (diglycerol and glycerol formal) were estimated from group contribution methods using CHEMCAD process simulation software. Vapor-liquid equilibrium compositions were estimated by CHEMCAD using the Soave-Redlich-Kwong equation of state.

CHEMCAD was used to design all of the process units except the TE reactor and diesel engine/generator set. The reactor was sized based on the residence time used in the laboratory experiments (3 minutes) to obtain nearly complete conversion of the SO, although extra volume was allowed to provide sufficient heat transfer area for heating the reaction mixture with the diesel engine exhaust gases. While designing distillation column D1, a small percentage of the reaction byproducts were allowed to remain in the bottoms product (BD) since we believe that some byproducts can be included into the BD. The percentage of the byproducts that can be included in the BD fuel is presently unknown and a somewhat arbitrary 1.62 % was included, which possibly could be higher. The remaining byproducts in overheads stream of D1 were separated from water in D2. Some of the byproducts may be valuable to be recovered and sold as separate products, although no credit is taken for these products in the preliminary estimate of the cost of manufacturing (COM). The diesel engine was sized to provide a sufficient amount of heat for the reaction and uses part of the produced BD (11.3 mol %) as fuel for the engine. The power from the engine is used to generate electricity that is to be sold to the local grid for $0.10/kWh.

The capital and total manufacturing costs for the process were estimated using the methods outlined in Turton et al. [2] and Ulrich [3]. All pieces of equipment with their bare module costs and the total fixed capital investment (FCI) have been considered in 2006 dollars.

The module cost for each piece of equipment includes the purchased cost of equipment and cost of piping, instrumentation, structural supports, etc. associated with the equipment as well as the labor cost for installation and indirect costs such as freight, insurance, engineering fees, and overhead. An additional 18% was added for contingency and for the contractor's fee. Carbon steel was specified for equipment exposed to temperatures less than 250°C and stainless steel was specified for equipment exposed to higher temperatures.

The raw materials costs are for the SO and the methanol. SO was assumed to be available for $2.10/gal [4]

and methanol at \$0.33/gal [5]. The utilities cost was taken from Turton et al. [2]. Because no waste was generated by the proposed technology, no cost of waste treatment was considered. COM was calculated as [2]:

$$COM = 0.2860\ FCI + 2.5755\ C_{OL} + 1.163(C_{UT} + C_{WT} + C_{RM})$$

The various other items in the COM, such as maintenance costs, supervisory and clerical labor, depreciation of the FCI, administration, distribution and selling, and R&D costs are estimated as fractions of the FCI, operating labor cost, utilities cost or raw materials cost. The cost of manufacture is given in Table 1, together with revenues from the sale of electricity, and the break-even cost of the net BD available for sale.

Table 1: Comparison of biodiesel cost for three options.

Option	BD Capacity (gal/day)	COM (\$/yr)	Electricity Revenue (\$/yr)	BD Cost (\$/gal)
Case 1[*]	2300	2,572,804	115,316	3.46
	4600	4,385,660	228,887	2.95
	9200	8,036,670	457,774	2.68
	12000	10,217,965	598,267	2.61
	15000	12,567,301	747,834	2.56
Case 2[*]	9200	7,908,132	-	2.59
Case 3[*]	9200	7,733,783	-	2.49

Case 1[*]: Byproducts separation and power generation;
Case 2[*]: Byproducts separation and fired heater;
Case 3[*]: Water separation and fired heater.

For the base case design of 2300 gal/day of BD, COM was estimated to be \$ 2,572,804/yr. The total electricity produced from power generator (with 40% efficiency) is 1,171,196 kWh/yr, but 18,036 kWh/yr are used to drive the methanol and SO feed pumps, leaving 1,153,160 kWh/yr available for sale. Assuming that the selling price of electricity is \$0.10/kWh, the revenue obtained from electricity would be \$ 115,316/yr. Hence the net COM was estimated to be \$ 2,457,488/yr. The total BD produced per year is 800,557 gal from which 11.4 % is used for generation of electricity by the diesel-generator; hence the remaining 88.6 % of BD available for sale is 709,774 gal/yr. Accordingly, the break-even cost of BD is (\$2,457,488/yr)/(709,774 gal/yr) or \$ 3.46/gal.

Most of the total cost of manufacturing comes from the raw materials and labor costs. Although little can be done to reduce the raw materials cost, the COM/gal of product would be significantly reduced for a larger sized plant since the number of operators would not change. Also some savings in capital cost would be realized with a larger capacity plant. Thus the COM for plant capacities of 4600 gal/day, 9200 gal/day, 12,000 gal/day, and 15,000 gal/day were calculated. As expected these led to reduced break even costs for the BD product of \$2.95/gal, \$2.68/gal, \$2.61/gal, and \$2.56/gal respectively.

A second alternative design taken into consideration was the use of a direct-fired *Dowtherm* heater fueled by the BD products to heat the TE reactor instead of exhaust gases from the diesel-generator. This option reduces the BD fuel needed for heating the reactants to only 3.0 % of the BD product, substantially reducing the cost of the BD. For a process producing 9200 gal/day of BD, the break-even cost is reduced from \$2.68/gal to \$2.59/gal.

Further reductions in cost also may be possible if more of the reaction byproducts can be used directly in the BD fuel. In the case that essentially all of the byproducts can be used and only the water must be separated from the reaction products, the quantity of BD fuel increases by 16.5 % and only a single distillation column is required. For producing 9200 gal/day of BD using this option, its cost is reduced to \$2.49/gal. This would be competitive with the current price of diesel fuel of ~\$2.60/gal. [6]

The options considered using the diesel-generator may be more attractive. This option is most suited for isolated locations when electricity is not readily available. Thus it would be competing with other diesel-generator options where the cost of power generated is much higher than \$0.10/kwh. A more appropriate number to calculate may be the cost of power generated by the diesel-generator if the BD can be sold for \$2.80/gal.

4.2 Soybean oil extraction

We are currently working on the optimized design and economics of SC-CO_2 extraction of SO. It is expected that the SCE cost will be significantly reduced by using a quasi-continuous extraction process with a battery of four extractors (one for loading/unloading) operated at 400 bar and 100°C. Compared to literature reported values of 600 bar and 80°C, the former conditions will lead to similar yield of SO but lower operating costs.

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