

**INTEGRATED MULTISTAGE SUPERCRITICAL TECHNOLOGY  
TO PRODUCE HIGH QUALITY VEGETABLE OIL AND BIOFUELS**

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## ABSTRACT AND KEY WORDS

A multi-step integrated technology to produce high quality vegetable oils and biodiesel fuels is proposed, documented for technical and economic feasibility, and preliminarily designed. The first step of the integrated system consists of soybean oil extraction with supercritical fluids. The second step is designated to transform the soybean oil into biodiesel through transesterification with supercritical methanol or ethanol. Part of the biodiesel is directly consumed by a diesel engine integrated in the system which, in turn, provides the mechanical power needed to pressurize the system as well as the heat of the exhaust gases, heat required for the extraction and transesterification steps. Different versions of this system can be implemented based on the main target of the technology implementation: oil and biodiesel production or diesel engine applications. Various process options considered for biodiesel fuel production estimate break even costs of biodiesel as low as \$ 2.56 per gallon with the diesel generator for a plant of 15000 gallon/day to \$ 2.49 per gallon for a plant of 9200 gal/day with a burner replacing diesel generator (taxes are not included). Both are competitive to the current price of ~\$ 3.0/gallon of diesel. Also, the efficiency of the diesel engine combustion and cleaner emissions render the proposed technology very attractive for the transportation sector when only the transesterification step is carried out just to provide superior fuels to diesel engines with minor engine retrofitting.

**Key words:** multi-step integrated technology; supercritical fluid extraction of soybean oil; oil transesterification with methanol/ethanol; biodiesel fuels.

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## **SUMMARY**

The project goals were to develop the necessary knowledge base to assess the possibility of a commercial technology for the coupled process of continuous soybean oil (SO) and biodiesel (BD) production using a supercritical alcohol. The soybean oil is extracted using supercritical CO<sub>2</sub> followed by transesterification (TE) with supercritical methanol to produce biodiesel. The biodiesel can be marketed and part of the product fuels a diesel engine power generator which produces electricity for remote usage and heat from the exhaust gases for transesterification reaction. The stage 1 objectives were successfully accomplished.

## **Section 1**

### **INTRODUCTION**

#### **BACKGROUND**

The recent run up in crude oil prices combined with disruptions in supply and refining capacity have driven the prices of motor fuels to new highs and created spot shortages throughout the world, including the United States, where post hurricane Katrina effects and Alaska Prudhoe Bay shutoff production are the most recent home examples. This unfortunate development is likely to remain a fact of life for years to come. However it has given new urgency to the development of alternative, renewable fuels that not only reduce the reliance on petroleum feedstock, but may also result in reduced emissions of airborne pollutants. Biodiesel (BD) derived from plant and 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 oil extraction from soybeans in multiple extractors and cascaded separators. The extraction step should use three parallel batch extractors with supercritical (SC) carbon dioxide (CO<sub>2</sub>), and multiple CO<sub>2</sub> recovery stages. The BD production step will use the extracted oil and a SC alcohol such as methanol and ethanol in a continuous tubular reactor and will not need catalysts and multi-step separations. The process will use a diesel generator to provide power and heat for the upstream processes.

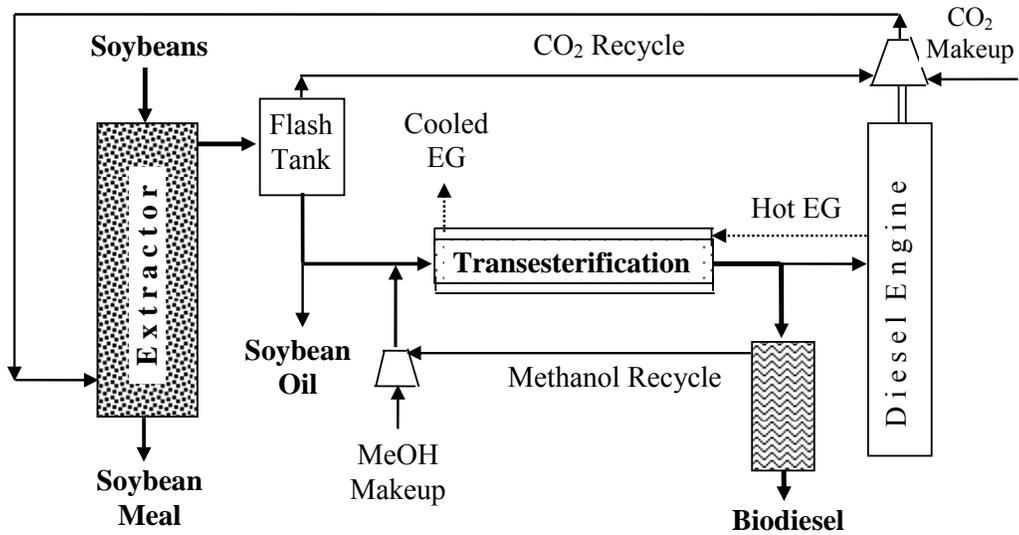
The proposed integrated system has a potential wide range of applications if implemented. First, it is very attractive for farmers since it reduces their dependency on high petroleum fuel prices. Many farmers who crop soybeans already use SO as a fuel. However, SO is not an acceptable fuel because of the harmful emissions and damage it renders to the engines, especially on long-term usage. Secondly, this system, without the SFE step, should have great potential to be implemented on transportation vehicles since only small retrofits of the diesel engines is required. All the needs for the TE reaction to proceed are already available around these engines, including the free heat of the exhaust gases.

#### **PROJECT GOAL AND OBJECTIVES**

The overall goal is to develop an industrial process for continuous soybean oil (SO) production, and couple that process to BD production using a SC alcohol (e.g., methanol and ethanol) as shown in Figure 1. Stage 2 would include design, construction, and operation of a pilot plant. Specific Stage 1 objectives were:

- 1) perform a literature survey for the component steps of the integrated system;
- 2) develop a conceptual design with key steps established for the integrated process;
- 3) determine optimal parameters for oil extraction and the reaction parameters and yields at lab-scale;
- 4) determine and compare economics with current methods.

All of the above objectives have been successfully accomplished.



**Figure 1. Schematic of an *Integrated Multistage Supercritical Technology System* to produce high quality Vegetable Oil and Biodiesel Fuel.**

## PROJECT TASKS

In order to achieve the proposed goals and objectives, the following tasks were carried out:

Task 1: Project Management

Task 2: Develop Business Plan/Stage 2 Research Plan Based on Stage 1 Achievements

Task 3: Literature Survey

Task 4: Conceptual Design

Task 5: Experimentation

Task 6: Revising Conceptual Design and Economic Analysis

**Section 2**  
**PROJECT DESCRIPTION**

**LITERATURE SURVEY**

A thorough search and survey (several hundred references from which we selected 123) have been performed on reported literature results and information regarding the individual processes in our proposed integrated multistage supercritical (SC) process to produce high quality vegetable oil and biofuels (e.g., BD). The literature survey includes a summary of methods and process conditions for the SO extraction and reaction to BD steps (Tables 1-2).

**Table 1. Selected references with processing conditions for SFE methods**

Authors; Journal	Title	Process Conditions*	Economic Analysis	Conclusions
E. Reverchon L.Sesti Osseo  JAOCS (1994) 71(9) 1007-1012	Comparison of Processes for the Supercritical Carbon Dioxide Extraction of Oil from Soybean Seeds	1. 80 °C 2. 600 bar 3. N/A 4. N/A 5. N/A 6. 66.5 T/hr 7. Variable 8. Dynamic	1. Without heat exchanger optimization network, operating cost is 3000 Arbitrary Units (AU) vs.1950 AU for hexane extraction process 2. For the process with heat exchanger optimization network, operating cost is 1000 AU (<1950 AU)	Plant cost using SC CO <sub>2</sub> extraction with heat exchanger optimization network was lower than that of conventional hexane extraction.
M.S. Kuk R.J. Hron, Sr.  JAOCS (1994) 71(12) 1353-1356	Supercritical Carbon Dioxide Extraction of Cottonseed with Co-solvents.	1. 80 °C 2. ~ 483 bar 3. 60 min. 4. <5 vol. % 5. 0 6. N/A 7. >98 % 8. Static	N/A	SC CO <sub>2</sub> yielded lighter colored oil as compared to conventional hexane. Cosolvent addition to SC CO <sub>2</sub> yielded darker oil due to extraction of gossypol
E. Stahl E. Schutz H. K. Mangold  J. of Agric. and Food Chemistry (1980) 28 1153-1157	Extraction of Seed Oils with Liquid and Supercritical Carbon Dioxide.	For SO: 1. 20 °C 2. 280 bar 3. 150 min. 4-6. N/A 7. 16.6 % 8. Dynamic	N/A	1. Concentration of oil in SCCO <sub>2</sub> was independent of CO <sub>2</sub> flow rate. 2. Yield of oil extracted with SC CO <sub>2</sub> was 16.6 % vs. 19.9% for hexane extraction
R. Eggers  Supercrit. Fluid Technology in Oil and Lipid Chemistry. Eds, J.W.King G.R. List; AOCS Press, Champaign, IL (1996), p. 35-65	Supercritical Fluid Extraction (SFE) of Oilseeds/Lipids in Natural Products	1. 40 °C 2. 750 bar 3. N/A 4. N/A 5. 20 kg CO <sub>2</sub> / kg seeds 6. N/A 7. 94 % for pressed cake; 82% for flakes 8. Dynamic	SFE of oilseeds required more energy for mechanical and cooling purposes, and less energy for heating purposes than the conventional hexane extraction process. High pressure oilseed processing will become economical only for continuous processing of oilseeds.	Refining the oil produced by SFE involves fewer steps as compared to the conventional hexane extracted oil.

\* 1-Extraction Temperature; 2-Extraction Pressure; 3-Extraction Time; 4-Cosolvent %; 5-CO<sub>2</sub> flow rates; 6-Capacity; 7-Degree of extraction; 8-Method.

**Table 2. Selected references with processing conditions for TE methods**

Reference	Title	Conditions*	Remarks/Observations	Conclusions
<b>Non Catalytic SC MeOH</b>				
H. Han W. Cao J. Zhang  Process Biochemistry 40 (2005) 3148–3151	Preparation of biodiesel from soybean oil using supercritical methanol and CO <sub>2</sub> as co-solvent	1. 280 °C 2. 150 bar 3. 24:1 4. 10 min 5. 98.5% 6. CO <sub>2</sub> :MeOH = 1:10 7. Soybean oil	1. High energy barrier for TE 2. For MeOH:oil<24, incomplete rxn; for MeOH:oil>24, high P 3. For CO <sub>2</sub> :MeOH<24, higher T required for the same yield. 4. At 300 °C, the reaction was complete in 5 min. 5. The reaction rate constants increased when CO <sub>2</sub> was added.	<b>Addition of co-solvent reduces the severity of the reaction conditions.</b>
D. Kusdiana, S. Saka  <i>Fuel</i> 2001 80: 693-698	Kinetics of transesterification in rapeseed oil to biodiesel fuel as treated in supercritical methanol.	1. 350 °C 2. 430 bar 3. 42:1 4. 2-4 min 5. 95 % 6. N/A 7. Rapeseed oil	1. SC MeOH brought the rxn mixture in a single phase 2. Higher ratio of MeOH:oil resulted in the increase in BDF 3. At 230 °C, the yield to ME was 70% in 1 hr; at 300 °C, 80% in 4 min; at 400 °C, 97 % in 2 min.	<b>At subcritical T&lt;239 °C, the reaction rates k &lt;0.0003 s<sup>-1</sup>, at 300 °C, k= 0.0071 s<sup>-1</sup> and at 350 °C, k= 0.0178 s<sup>-1</sup>. (the rate constant increased by a factor of 85 at T=350°C)</b>
D. Kusdiana, S. Saka  <i>Bioresource Technology</i> 2004 91: 289-295	Effects of water on biodiesel fuel production by supercritical methanol treatment.	1. 350 °C 2. 430 bar 3. 42: 1 4. 1-4 min. 5. 97 % 6. Methanol containing 10-36% of water 7. Rapeseed oil	1. For alkali catalyzed method, the conversion to ME was reduced in the presence of water (at 5% water, to 75 %) 2. For acid catalyzed method, the conversion was affected severely (at 5 % water to <5%) 3. For SC MeOH, conversion was 97 % for any water content.	<b>Supercritical method produced very high conversion to ME irrespective of the water and FFA content in oil, whereas in acid and alkaline catalyzed method conversion was reduced significantly as water or FFA content increased.</b>
<b>Base Catalyzed Transesterification</b>				
R. Alcantara J. Amores L. Canoira E. Fidalgo M.J. Franco A. Navarro  Biomass and Bioenergy, 18 (2000) 515-527	Catalytic production of biodiesel from soy-bean oil, frying oil and tallow	1. 60°C; 2. 1 atm 3. 7.5:1 4. ~30 min 5. 95 %; 6. NA 7. Soybean oil 8. < 0.5 % 9. MeOH 10. CH <sub>3</sub> ONa 11. 1% 12-15. N/A	1. 100% conversion claimed 2. Basic catalyst reused 3. Complete conversion in 1 hr 3. 95% conversion in 3 hrs for tallow fat with 1% base catalyst 4. Cetane index for used soybean oil was 49 5. Soaps formed were broken by use of concentrated HCl.	1. Results are interesting but contradictory to literature 2. Water purification step not provided 3. Excess MeOH separation from both phases by vac. distillation 4. Information on free glycerin not provided
M. Cetinkaya F.Karaosmanoglu  Energy&Fuels 2004, 18, 1888-1895	Optimization of base-catalyzed TE reaction of used cooking oil	1. 55°C; 2. 1 atm 3. 3:1 and 6:1 4. 4.5 and 0.5 h 5. 100 % 6;12-13;15. N/A 7. Cooking oil 8. 0.62 % 9. CH <sub>3</sub> OH 10. NaOH 11. 1 and 2% 14. 7stages	1. 100% conversion claimed 2. No information on catalyst reuse 3. NaCl is present in glycerin phase in trace amounts 4. For 28% nonglycerin organics in glycerin phase, if methanol has to be recovered, separation steps will be required	1. Rxn products were tri-, di- and mono-glycerides, BDF, glycerol, and MeOH 2. Overnight settling time is required after ester phase washing 3. Hot water for washing ester phase was 1:1
F.Karaosmanoglu K.B.Cıgızoglu M. Tuter S. Ertekin	Investigation of refining step of biodiesel production	1. 65°C; 2. 1 atm 3. 6:1 4. 5. 38 min 5. 97.32 %	1. Decantation of the reaction products required 2. Three schemes for product refining are described	Method of washing with hot distilled water at 50 °C gave the best results.

Energy & Fuels 1996, 10, 890-895		6, 12, 15. N/A 7. rapeseed oil 8. 0.07 % 8. 0.16 % 9. CH <sub>3</sub> OH 10. NaOH 11. 6% 13. 5 hrs 14. 5 stages	3. Methanol was evaporated from ester phase in rotary evaporator 4. Glycerin phase was washed in 3 stages with distilled water (20 °C) 5. Ester phase was washed with hot distilled water at 50 °C	
Acid Catalyzed Transesterification				
S. V. Ghadge H. Raheman  Biomass and Bioenergy 28 (2005) 601-605	Biodiesel production from mahua oil having high free fatty acids	1. 60°C; 2. 1 atm 3. 6:1 4. 30 min 5. 98 % 6, 12, 14. N/A 7. Mahua Oil 8. 19 % 9. CH <sub>3</sub> OH 10. KOH 11. 0.7% (w/v) 13. overnight 15. 2	1. No information about downstream processing of alkaline TE products 2. During acid treatment, each step required separation of 2 phases 3. Flash point is unusually high, without water wash step, seems to be skeptical	1. High MeOH% was required in the acid treatment 2. At each step of acid treatment excess MeOH can be obtained by fr. distillation 3. Water must be removed from product mixture during reaction, as water is not desirable in subsequent alkaline TE 4. Downstream separation of alkaline TE products required
J. Hancsók F. Kovács M. Krár  Petroleum and Coal, (2004) 46(3), 36-44,	Production of vegetable oil fatty acid methyl esters from used frying oil by combined acidic/alkali TE	1. 60 °C 2. 1 atm. 3. 4:1 4. 2 hrs 5. 60 % 6. THF/ Dioxane 7. Frying oil 8. 32.5% 9. MeOH 10. MeONa 11. 3 % 12-14. NA 15. 1	Complicated method of reaction product separation at each step	1. For oils with FFA>0.5%, acidic pretreatment was necessary. Oil with 32.5% FFA required 6 h of pre-TE treatment in absence of tetra-hydrofuran (THF) 2. Acidic+alkaline process took 6 h with THF 3. For HFFA+sun flower oil when FFA was >13%, preacidic TE was faster with THF; for the total TE, a yield>96.5% was reached for a time of 4-6 h

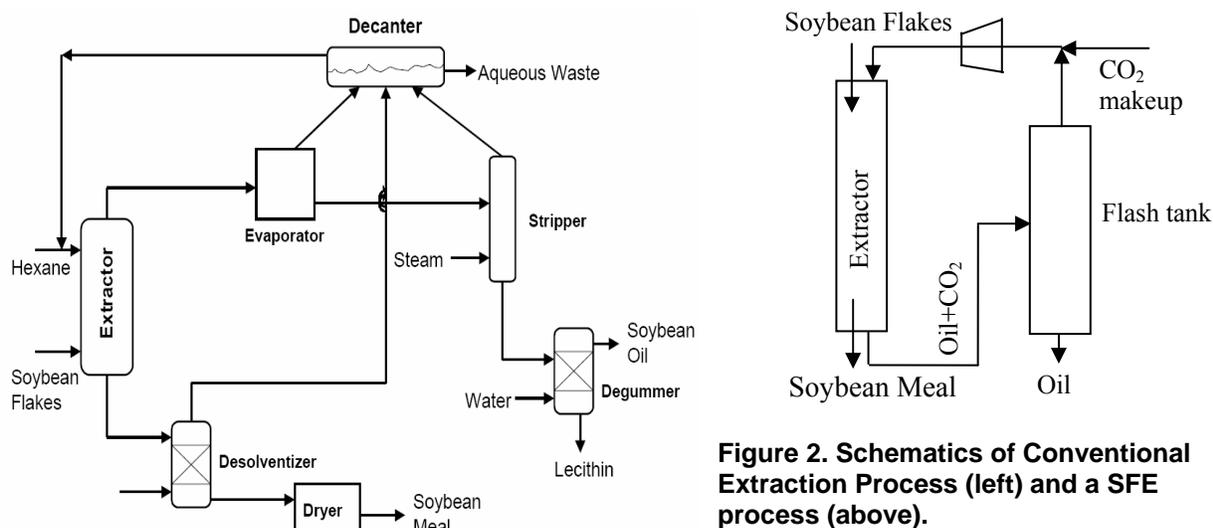
\*Process Conditions: 1-*T* in °C; 2-*P* in bar/1 atm; 3-Alcohol:Oil (molar); 4-time in min. for TE completion; 5-% yield of Methyl Esters/BD; 6-solvent/cosolvent; 7-oil used; 8-free fatty acids (FFA) % in oil; 9-alcohol used; 10- Catalyst; 11-Catalyst concentration (wt %); 12-water wt. % for washing; 13-separation time for ester/glycerol phase; 14-stages required for water washing of products/ester/glycerol phase; 15- No. of steps to reduce the FFA to a reasonable level.

Also, a description of the advantages and limitations of the coupled processes, with emphasis on information regarding methods to improve the overall cost of the targeted products is provided for the selected references. Based on the main processes involved in the integrated technology the literature information on SC extraction (SFE) [A1-A19] and transesterification (TE) [B1-B15] is accordingly grouped with secondary groups regarding SO solubility in different solvents/cosolvents [C1-C24] and conventional TE [D1-D7; E1-E10]. Finally, a list of references on general aspects related to SO and BDF is provided [F1-F43].

SO is an important product of one of the two major agricultural crops grown in the Midwest and, locally, in the Finger Lakes area of NY State (soybean and corn). Raw soybeans contain ~20% oil and the conventional process uses hexane to extract the oil. Unfortunately, the hexane also extracts the phospholipids (~40% in soybeans), that have to be

washed out of the oil in a later processing step called "degumming." In addition, the hexane removes high molecular weight species that cause the unrefined oil to be dark brown in color. The environmental problems with the conventional process center on the use of hexane from which the dark oil is cleaned up by an adsorbent (e.g., diatomaceous earth). The spent adsorbent is customarily landfilled resulting in pesky fires due to inevitable content of hexane, which is volatilized in the warm summers. Also, some hexane is emitted directly from the process to the atmosphere often generating explosions at soybean processing plants.

From the literature referring to SFE processes of SO extraction [A1-A19], we selected representative references as summarized in Table 1. While it is considered by some of the researchers that SFE of SO from soybeans is too costly compared to conventional extraction with liquid hexane, there are few reported studies showing that an optimized SFE process can be designed to be cost effective. Representative schematics of the two technologies (Figure 2) show the simplicity of the SFE process compared to conventional SO extraction by liquid hexane.



**Figure 2. Schematics of Conventional Extraction Process (left) and a SFE process (above).**

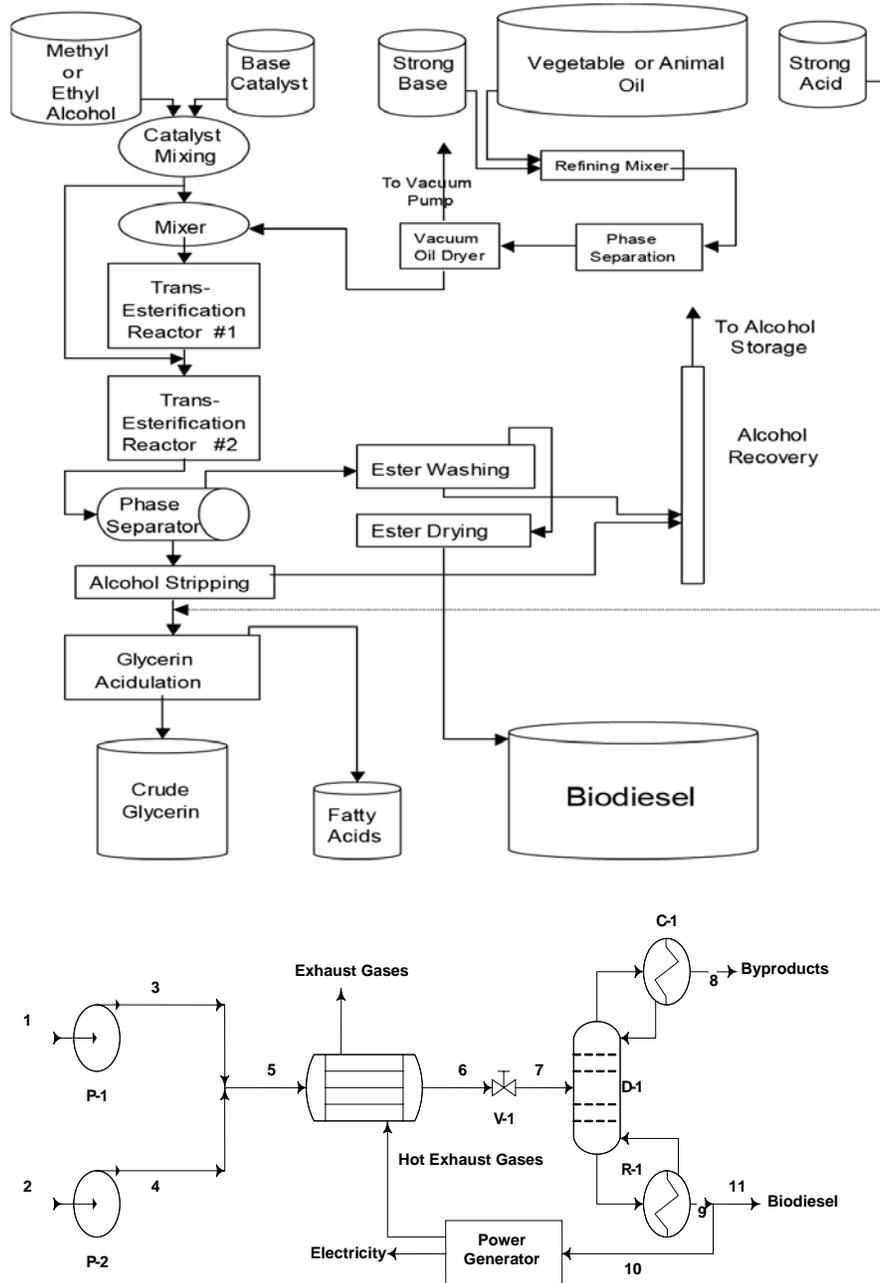
SC CO<sub>2</sub> is very effective in extracting oils from a variety of oilseeds, devoid of any appreciable amount of protein content. Although not yet commercially attractive, SC CO<sub>2</sub> can be used to extract SO from soybeans instead of hexane, which is volatile and highly flammable. The oil extracted from soybeans with SC CO<sub>2</sub> is of much higher quality than the hexane-extracted oil. It does not contain any phospholipids, thus eliminating the degumming step. Also, higher molecular weight species are left in the beans, yielding clear, light-colored oil without further processing. The reported disadvantage of CO<sub>2</sub> is that very high pressures (600-800 bar) are required to achieve sufficiently high oil solubility. However, our experience in this field led to a 90% SO extraction yield at 400 bar and up to 100 °C. Finally, the transport of the crushed soybeans at high pressure would be quite difficult and the actual implementation of this process would hinge on the successful scale-up of a high pressure continuous extraction process.

In an example [A1], initial SC CO<sub>2</sub> extraction of soybean flakes was performed at 320 bar and 80 °C to extract the oil, leaving the proteins in the defatted flakes. A 2<sup>nd</sup> step was then performed on the soybean matrix using ethanol as cosolvent ( $X_{et}=0.10$ ), varying the pressure from 166 to 689 bar and the temperature from 60 to 80 °C. The positive

results have remarkable interest because the conventional extraction with liquid hexane leaves ~50% of the total phospholipids in the spent seed matrix. In another recent study [A5], the authors claimed that an effective SO extraction has been achieved at 300 bar and 40 °C with a SC CO<sub>2</sub> flow rate of 1.8 STP L/min. The yields obtained were similar to those obtained by hexane extraction, but the quality of SO extracted by SC CO<sub>2</sub> was superior. The authors concluded that the SO extracted by a SFE process could compete with that obtained by the conventional extraction since the oil refinement stages are simplified significantly and the solvent distillation stage is completely removed (the two most costly steps in terms of energy consumption). In another example [A6], Sievers performed an energy optimization of SFE processes and recommended a separation step SO-SC CO<sub>2</sub> up to 150 bar to save in the cost of pumping energy. The calculated energy costs together with data for SO/CO<sub>2</sub> (w/w) can form the basis for designing an economically optimized SFE plant. In a detailed and comprehensive analysis of SO extraction by SC CO<sub>2</sub> [A9], Reverchon et al. concluded that an optimized extraction network including several heat exchangers can render this process technically feasible and economically competitive with conventional SO processes. The authors claimed that the most efficient SFE version to extract SO with SC CO<sub>2</sub> was based on an isobaric scheme wherein the SO extracted was separated only by changing the temperature in the separator. In a further improvement, the authors added a heat transfer network under the most favorable energy usage. Operating costs were considered on an industrial scale to select different alternatives and for one of these the costs fell in the same range as for conventional extraction plants.

From the reported results on TE processes [B1-B15], the following references appear to be closer to our intended BDF production. In one example [B3], refined or pure SO was treated with SC methanol and CO<sub>2</sub> as a co-solvent at 280 °C, 143 bar in a batch reactor for 10 minutes residence time. Under these conditions, 98.5% conversion of oil to BDF was achieved. The other key process variables were molar ratios of methanol to oil (24:1), and CO<sub>2</sub> to methanol (1:10). At these process conditions, glycerol was present in the reaction products which were settled for 60 minutes for the separation of the two phases. Then methanol was evaporated from both phases at 70 °C. Also, canola oil was treated with SC methanol in a capillary reactor at 450 °C, 400 bar for 4 minutes [F15]. The methanol to oil ratio was from 1:2 to 2:1(v/v). On molar basis, the range of methanol to oil ratio was from 11:1 to 45:1. The excess methanol was removed using the rotary evaporator at 45 °C and 10 KPa. Thermal decomposition of glycerol was reported for temperatures in excess of 400 °C at 400 bar. This decomposition will be helpful to overcome the problem of recovery of glycerol in the separation/purification steps. Also, with the demand of BDF likely to increase in coming years, enhanced BDF production would lead to more glycerol formation. There is already ample glycerol supply in the market and the demand of glycerol is not likely to increase significantly, especially from this source wherein its purification is not very advanced. Buhler et al. [B15] reported the decomposition of glycerol in near and SC water under several sets of conditions. At 452 °C and 450 bar, the two main products of glycerol decomposition were acetaldehyde and acrolein. Acid catalysts (H<sub>2</sub>SO<sub>4</sub>) at 300 °C and 345 bar similarly decomposed glycerol to acetaldehyde and acrolein. Glycerol also decomposed to these products at 356 °C and 450 bar in the absence of acid catalysts. Wataru et al. [F15] assumed that glycerol will decompose by SC methanol ionic reaction citing the example of decomposition of glycerol in SC water. However, these ideas are very speculative and needs systematic experimental investigation. It could be also inferred from the reference [F15] that the methyl linoleate starts

decomposing at 390 °C. The decomposition products of methyl linoleate and glycerol were not reported in this paper. Fuel properties of BDF in presence of these decomposition products must be studied to fully evaluate the option of decomposition of glycerol. To outline the significant difference between TE technologies, Figure 3 shows two representative schematic diagrams of the processes involved in BDF production at industrial scale. The simplicity of the proposed SC TE process is apparent.



**Figure 3. Schematics of a base-catalyzed TE (top) and SC TE (bottom). P-1, P-2: Rotary Positive Displacement Pumps; H-1: Shell and Tube Heat Exchanger; V-1: Pressure Reduction Valve; D-1: Distillation Column; C-1: Condenser; R-1: Reboiler.**

In conclusion, due to increasing demand and an increase in usage of SO, the oil industry is processing more oil than ever before and SO is the most processed, consumed and exported oil in the United States [C3]. SO provides food for humans and animals and material for many industrial uses (e.g., BDF). For decades, the industry has used the same basic principles to extract oil from oilseed and process crude edible oil. The new goal is to utilize advances in technology to extract, refine and develop oil products into something better, faster, and cheaper. The new developments in the field point toward more energy-efficient and cost-effective technologies to extract and to process this highly valuable commodity to more value-added commercial products. Our survey shows the high potential of the modern, integrated research to generate technically feasible and economically competitive alternatives to the environmentally harmful conventional methods. The market for BDF in New York is substantial and is rapidly growing as it was presented in a comprehensive report for NYSERDA [F12]. This literature survey is intended to present the major findings on the technical and economic feasibility of creating a modern alternative to the BDF industry in the United States and in New York State in particular.

### **CONCEPTUAL DESIGN**

The results of the above literature survey have been used for a preliminary conceptual design of the integrated and coupled processes of SFE and TE interconnected to a diesel engine for clean combustion of the TE products and mechanical and electrical energy supply to the proposed processes (Figure 1). The most advantageous steps on the grounds of both technical and economical performance have been considered.

For the *extraction step*, the reported results corroborated with our own experimental information to show that SFE of SO requires high pressures (beyond 400 bar, with our results suggesting the lower limit of this range) and relatively high temperatures ( $>80\text{ }^{\circ}\text{C}$ , with our optimum yield at  $\sim 100\text{ }^{\circ}\text{C}$ ) for acceptable high efficiencies of oil recovery when pure SC  $\text{CO}_2$  is used. However, under these conditions, appropriate process optimization, especially regarding the energy rational usage, can render this method competitive with the conventional extraction with liquid hexane [A9]. Further, 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.

In the *transesterification step*, we want to prepare BD from SO in SC methanol/ethanol. The conditions at which bulk glycerol decomposed in our reaction system have been determined as  $350\text{--}400\text{ }^{\circ}\text{C}$  and  $100\text{--}300\text{ bar}$ . But we expect the conditions to be less severe when using co-solvent  $\text{CO}_2$  in our system. By utilizing the data of the yield of reaction versus reaction temperature (from [B3]), we can calculate the energy of the activation and rate constant of the reaction. Here we assume that the reaction is pseudo first order and the reverse reactions are not significant. These assumptions were made for the design purpose as we are using a stoichiometric alcohol to oil molar ratio of 3:1. The data from the reference #B3 fit reasonably well to our assumptions. So far, the kinetics and reaction mechanism have not been reported for the TE of SO in SC methanol and  $\text{CO}_2$ . Also, the kinetics and mechanism of degradation of glycerol is not

yet clear. Hence, we propose to design and compare two processes, one with glycerol formation and the other with glycerol decomposition at the process conditions of 350-400 °C, 100-400 bar. 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. For a BD plant, different capacities from 9,200 up to 15,000 ton/year, with plant running for entire year, will be chosen for an economic analysis.

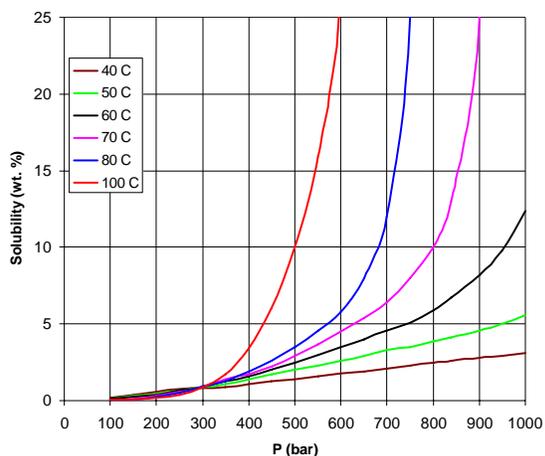
In conclusion, a conceptual design for the integrated steps of extraction and TE, including a diesel engine as a source of energy, is schematically shown in Figure 1. Further details of the TE step are outlined in the flowsheet shown in Figure 3 (bottom). Updated modifications will be operating as the proposed research should progress in stage 2.

## EXPERIMENTATION

### 1. Laboratory Scale SFE of Soybean Samples

Experimental activity was focused on extraction rate experiments since successful interpretation and modeling of the experimental extraction data are essential for the design, optimization, and scale-up of SFE processes.

**1.1. Samples Acquisition.** Soybeans have been obtained from a farm on the shores of the Skaneateles Lake, NY. Also, samples of crushed soybeans, previously roasted, have been acquired from The Sheppard Grain Co. during a trip to the site. A discussion with the company's manager, Mr. Sheppard, outlined his interest in our project and we will share with him the results of this phase of the project and possibilities for further interactions during stage 2.



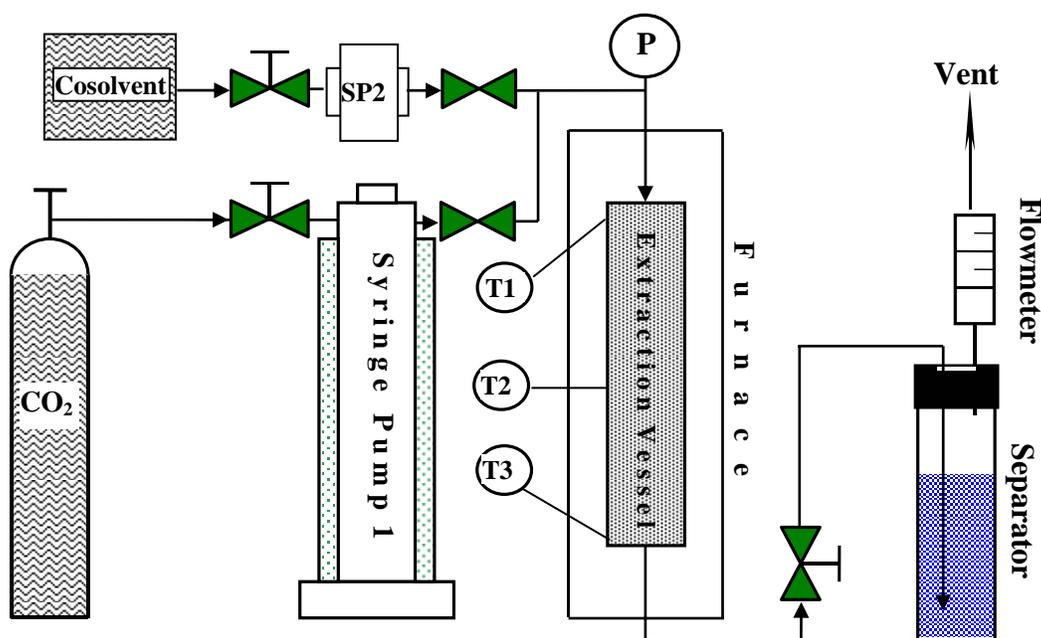
**Figure 4. Solubility of soybean oil in SC CO<sub>2</sub>.**

**1.2. Solubility of SO in SC CO<sub>2</sub>** shows the maximum capacity of this SC fluid to dissolve SO. Based on the overall reported data on this topic, we built a solubility dependency on the extraction *P-T* conditions (Figure 4). The SO solubility is strongly dependent on both temperature and pressure. Since the soybeans are currently roasted at 120 °C, an extraction temperature close to this value may be used to increase the yield of extraction. However, high values of pressures render this process economically unattractive. Optimized extraction conditions are required for a cost effective SFE.

**1.3. Laboratory Scale Extraction Experiments.** The ultimate goal of this study was to suggest a process to remove as much as possible of the SO content in a cost effective manner. The objectives of the laboratory scale SFE experiments were to investigate effects of various operational variables on the extraction process, define proper operating conditions for larger scale studies, and obtain data for extraction rate modeling. As SFE processes have been studied previously in the SU laboratory [A3; F16; F39-F43], the effects of temperature, pressure, SCF flow rates, co-solvent, and particle size on SO extraction rates were considered the major factors affecting extraction efficiencies.

Both the type and the presence of co-solvents in SC-CO<sub>2</sub> can affect SFE rates and efficiencies significantly and it was indicated that methanol could have been the best co-solvent among those investigated for SFE processes. However, our experiments proved that both methanol (10 vol. %) and hexane (5 vol. %) interfered with protein content in soybeans. Yet, the lower molecular hydrocarbons like propane and butane should be considered for further investigations. It is to be noted that propane is a good solvent for vegetable oils and it was used as a cosolvent during the transesterification process with SC methanol. The effectiveness of the SFE on SO extraction has been proved experimentally in this stage of the research for the case of SC CO<sub>2</sub> under conditions of 400 bar and near 100 °C.

**1.2.1. Apparatus.** Figure 5 is a schematic of the laboratory scale SFE unit with 50 mL volume of the extraction cell. A small dead volume is important because it allows almost instant pressurization of the system and consequently reduces the startup and shutdown effects on extraction data. The ability to obtain extraction data from the collection and analysis of effluent SO streams speeded up the data acquisition processes significantly and yielded better quality data.



**Figure 5. Schematic of Laboratory Scale SFE Unit.**

High pressure CO<sub>2</sub> and MeOH were delivered by two syringe pumps (ISCO, Inc.). A 50 mL fixed bed extractor (Thar, Inc.) was housed in an electrical furnace. The temperature of the system was monitored and controlled by several thermocouples with automatic data recording (National Instruments). The pressure was monitored by a Heise digital pressure indicator. The flow direction of SCFs is from top to bottom through the bed. A very fine micrometric valve was used to control the stream flow rates through the reactor and to depressurize the SCFs.

**1.2.2. Experimental conditions.** All the SO extraction experiments have been conducted on air-dried soybean matrices of different particle size ( e.g., whole grains, coarsely crushed beans, sieved crushed beans and finely ground soybean powder. Pressure, temperature, flow rate of SCFs and particle size were the operating parameters that significantly affected the efficiency and, hence, the operating cost of the SFE processes. Both moderate pressure

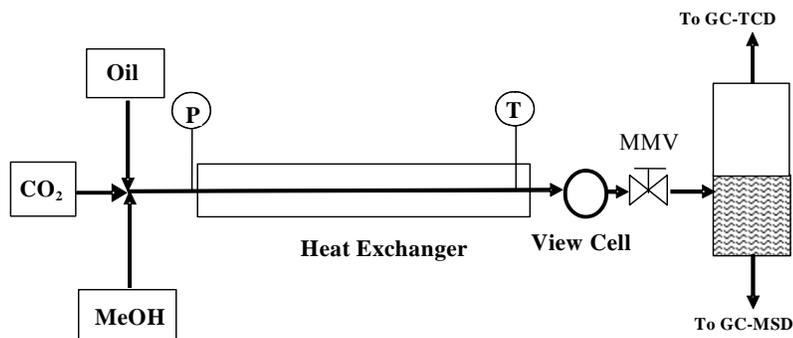
(100-400 bar) and temperature (50-80°C) were used in this study to permit reductions of processing costs. Relatively small SCF flow rates were tested to investigate the minimum flow rate allowed for effective SO extraction which is advantageous to reach the saturation level of the SC CO<sub>2</sub> and lower pumping costs for a commercial SFE process. Screening experiments to select the optimal parameters for the oil extraction from soybeans have been performed in the laboratory apparatus shown in Figure 5. The appropriate values of temperature and pressure (*T-P*), flow rates, and a suitable co-solvent to be used along with SC CO<sub>2</sub> were selected (Table 3).

**Table 3. Experimental conditions for the extraction of soybean oil**

Matrix	CO <sub>2</sub> FR mL/min	Cosolvent FR mL/min	T °C	P bar	Extraction time minutes	Yield Wt %	Comments
Whole soybeans	2.00	-	100	400	35		Low yield
Whole soybeans	2.00	0.2; MeOH	100	400	35		
Crushed soybeans	3.00	-	80	400		10	yield of 1/2
Crushed soybeans	2.00	0.1; hexane	125	400		19	
Soybean powder	2.00	-	100	400	30	18	
Soybean flour	-	Batch extraction with liquid hexane	25	1	1200	18	

## **2. Laboratory Scale Transesterification of Soybean Oil**

Experiments in tubular and batch reactors (Table 4) have been executed to establish the optimal conditions of *P-T*-Composition and residence time under which the highest yield of BDF is obtained with minimum costs of energy and separation/purification. The designed apparatus (Figure 6) consists of two syringe pumps (ISCO) for SO and methanol/ethanol; tubular reactors (coiled Hasteloy pipes of 4 and 6 m length and 1.5 mm I.D.), heated in an electrical furnace; a view cell to monitor phase transitions; and a separator for BDF and gaseous TE products.



**Figure 6. A schematic of the laboratory flow apparatus to study phase transitions and TE.**

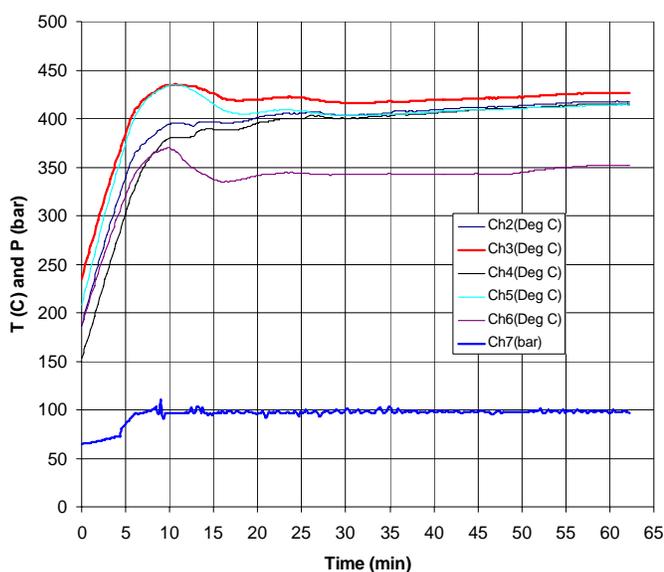
Using a high pressure view cell as a diagnostic aid, it was found that the oil miscibility with methanol is crucial to attaining a high conversion to the BDF. Experiments have been carried out with this apparatus to test its capabilities regarding SO-MeOH miscibility and phase transitions under different *P-T* conditions (Table 4 and Figure 7). The results for equal volumes of SO and MeOH heated in the view cell in a batch mode are shown in Figure 8. In this case, SO and MeOH 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. This kind of experiment is very important because complete TE reactions can be achieved, in a reasonable short time, only under complete miscibility conditions.

**Table 4. Laboratory experiments for TE reactions under different conditions**

Run #	System	T/°C	P/bar	FRoil/(mL/min)	FR <sub>ROH</sub> /(mL/min)	Rxn time/s	Comments
01TE	SO-MeOH	350	200	4.00	1.00	62	2 phases
02TE	SO-MeOH	400	200	4.00	1.00	62	2 phases
03TE	SO-MeOH	350	200	2.00	0.50	100	Clear, one phase
04TE	SO-MeOH	400	200	2.00	0.50	100	2 phases
05TE	SO-EtOH	400	200	2.00	0.50	120	Clear, one phase
06TE	SO-EtOH	400	200	2.00	0.40	120	Clear, one phase
07TE	SO-EtOH	400	100	2.00	0.40	186	No preheating
08TE	SO-EtOH	400	100	2.00	0.40	186	With preheating; clear
09TE	SO-EtOH	400	100	2.00	0.40	186	With preheating; clear
10TE	SO-EtOH	400	300	2.00	0.40	186	With preheating; clear
11TE	SO-EtOH	400	300	2.00	0.40	186	With preheating; brown
12TE	SO-EtOH	400	300	2.00	0.40	186	With preheating
13TE	SFO-EtOH	375	100	2.00	0.40	186	With preheating; clear
14TE	SFO-EtOH	400	200	2.00	0.40	186	With preheating; clear
15TE	SFO-EtOH	425	300	2.00	0.40	186	With preheating; clear
16TE	SFO-EtOH	425	100	2.00	0.40	186	With preheating
17TE	SO-MeOH	400	100	2.22	0.28	186	2 phases; brown
18TE	SO-MeOH	400	100	2.00	0.50	186	Clear, one phase
19TE	SO-MeOH	400	100	1.82	0.68	186	Clear, one phase
20TE	SO-MeOH	400	100	1.67	0.83	186	2 phases
21TE	SO-MeOH	400	100	1.50	1.00	186	2 phases
22TE	SO-MeOH	26-420	1-117	3 mL SO+3 mL MeOH			Batch phase transitions
23TE	SO-MeOH	327-425	125	0.8	0.1		2-3 phases
24TE	SO-MeOH	434-441	125	0.8	0.1		Clear, 1 phase
25TE	SO-MeOH	444-480	150	0.8	0.1		Clear, 1 phase
26TE	SO-MeOH	484-503	250	0.8	0.1		Clear, 1 phase
27TE	SO-MeOH	109-248	250	0.7	0.1		2 phases
28TE	SO-MeOH	244-249	250	0.1	0.1		2 phases
29Te	SO-MeOH	254-314	150	0.1	0.1		2 phases
29TE	SO only	27-400	100	0.10	0.00		Coking occurs at 400 °C

Typical TE conditions are shown in Figure 7.

**Figure 7. Typical P-T conditions for the TE reactions of SO-MeOH (runs 17-21 in Table 4). The thermocouples from channels 2-6 were located at different positions along the reactor: inlet (Ch6), outlet (Ch3), and near the middle (Ch2, Ch4, and Ch5). Only Ch3 was in the flowstream, inside the reactor.**



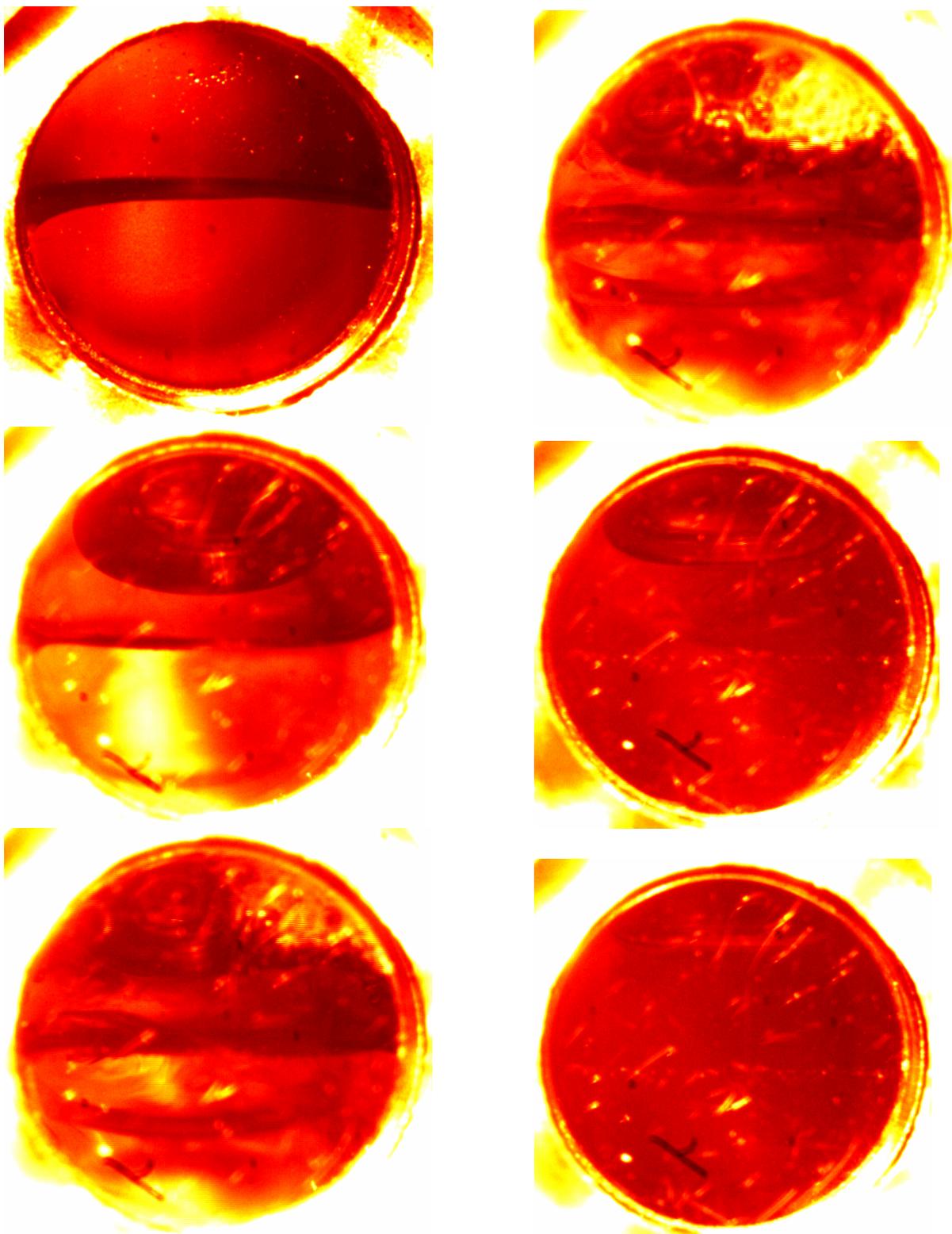


Figure 8. Selected photographs of phase transitions associated with TE reactions between SO and methanol (3 mL each; 1:25 molar ratio) heated from ambient room  $T$ - $P$  conditions to 420 °C and 120 bar. The images have to be seen down the columns from SO(L)-MeOH(L) (#1), through SO(L)-MeOH(L)-MeOH(V) (#2-3), SO-BDF-MeOH(L-SC) (#4-5), and then BDF-MeOH(SC) (#6).

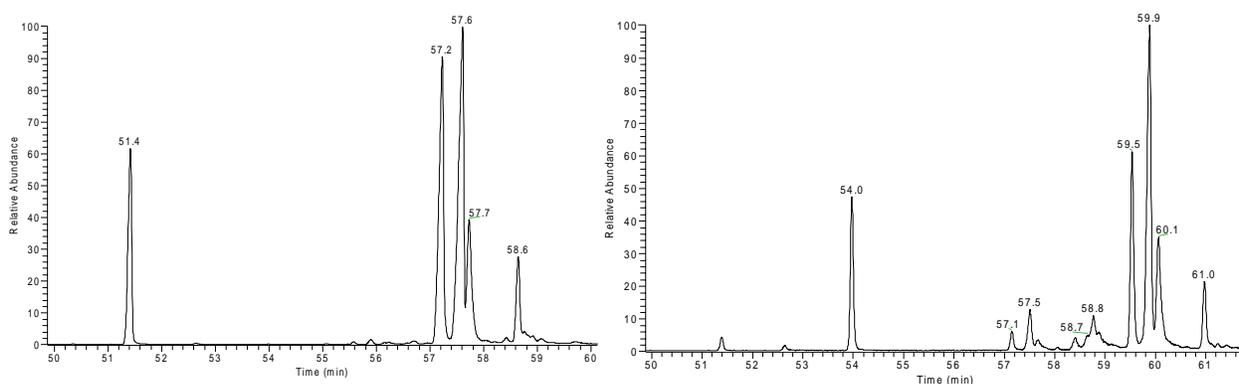
### 3. Enabling activities

Various enabling activities have been carried out to analyze the compositions of the initial materials and of the extraction/TE processes. Further analysis in conformity with the ASTM standards will be performed for the TE products. The quality of the extracted soybeans for feed purposes has to be assessed during stage 2 of the project.

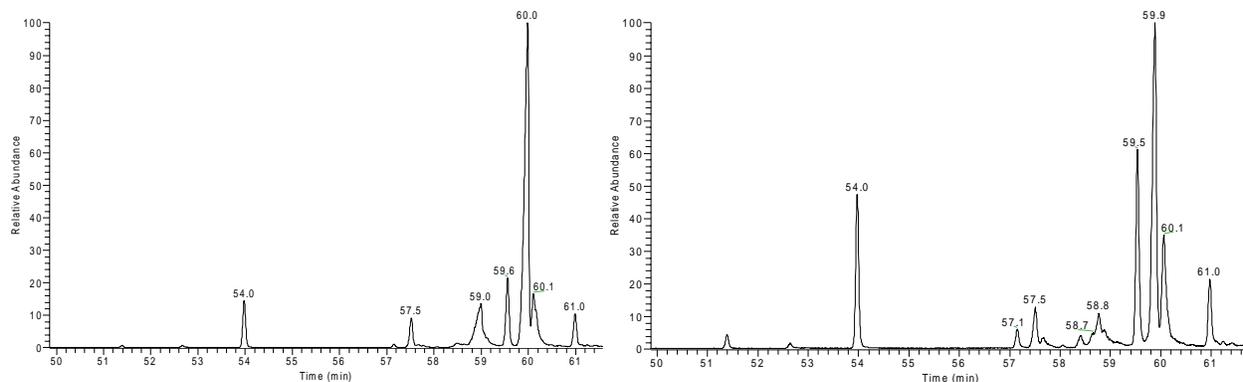
The concentration of SO components in the sample vial of the SFE step as well as the reaction products of the TE were analyzed by a Thermo Electron gas chromatograph (GC) equipped with a splitless injector, a MS detector (MSD), and an ultra performance capillary column (MS1, cross-linked 5% Ph Me silicone, 30 m × 0.20 mm I.D., 0.33 μm film thickness, Agilent, Inc.) (Table 5 and Figures 9-11). These figures are selected chromatograms which show the differences among the reaction products when different alcohols were used in the TE process (Figure 9), a comparison between the TE products when different oils were used (e.g., SO and sunflower oil) (Figure 10), and a comparison between typical TE products obtained with SC methanol and those in a commercial biodiesel sample (Figure 11).

**Table 5. Main Peak assignment in the chromatograms of Figures 9-11.**

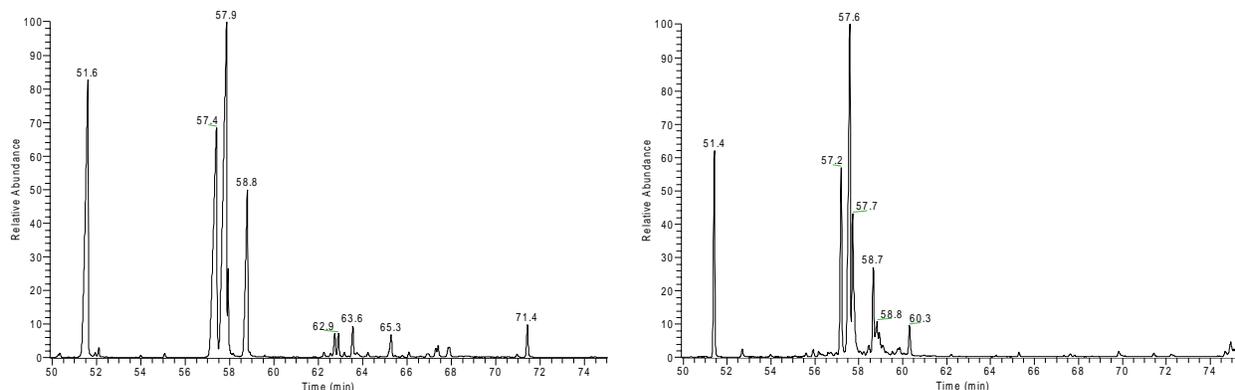
Retention Time (min)	Compound
51.4-51.6	Palmitic acid methyl ester; saturated
54.0	Palmitic acid ethyl ester; saturated
57.1-57.4	Linoleic acid methyl ester; unsaturated
57.5-57.6	Oleic acid methyl ester; unsaturated
57.7	Linolenic acid methyl ester; unsaturated
58.6	Stearic acid methyl ester; saturated
59.5-59.6	Linolenic acid ethyl ester; unsaturated
59.9-60.0	Oleic acid ethyl ester; unsaturated
60.1-60.3	Linolenic acid ethyl ester; unsaturated
61.0	Stearic acid methyl ester; saturated



**Figure 9. A comparison between TE products of soybean oil with MeOH (left) and EtOH (right). While small peaks for methyl esters are still shown in the latter, there is a shift toward the right for the ethyl-esters.**



**Figure 10. A comparison between TE products of sunflower and soybean oils with EtOH (left and right, respectively). The level of the saturated esters is lower for the sunflower oil products (peaks at 54.0 and 61.0 minutes).**



**Figure 11. A comparison between samples of a commercial biodiesel (left) and TE products from our experiments (right). It has to be observed: the lower level of the saturated esters in the latter (peaks at 51.4/51.6 and 58.7/58.8 min) and more byproducts in the former (peaks of 62-72 min).**

## REVISED CONCEPTUAL DESIGN AND ECONOMIC ANALYSIS

### 1. Revised Conceptual Design.

On the basis of the results of the above experiments correlated with the reported literature data, the preliminary conceptual design of the integrated technologies developed earlier was revised accordingly. Special emphasis was placed on the most beneficial connections of the involved processes and hardware components that lead toward a compact system that can produce the desired products in a cost effective manner.

Several options of the proposed integrated system have been considered, analyzed based on potential applications.

1.1. If a stationary plant is envisioned to produce SO and BD fuels, then the preliminary conceptual design is the suitable choice (figure 1).

1.2. Another option is based on the applicability to mobile diesel engines used on road and off road vehicles and targets only the production of BD from SO and an alcohol necessary to run the engine.

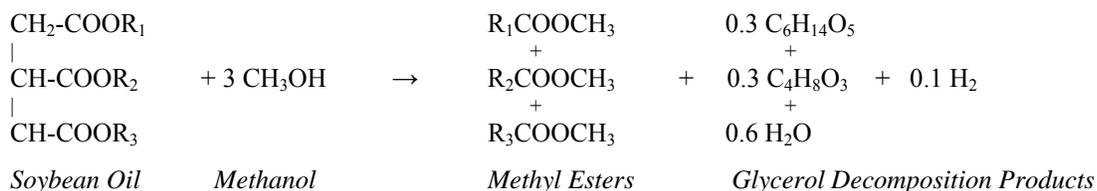
1.3. Only the TE step can be used to produce BD from any available source of SO while only a fraction of BD is consumed to run a stationary diesel engine (e.g., a power generator).

## 2. Economic Assessment.

Economic estimates for different system configurations were performed to select the most desirable configuration based on maximum benefits. For Stage 1, a system that produces biodiesel and soybean oil competitively with conventional processes was targeted.

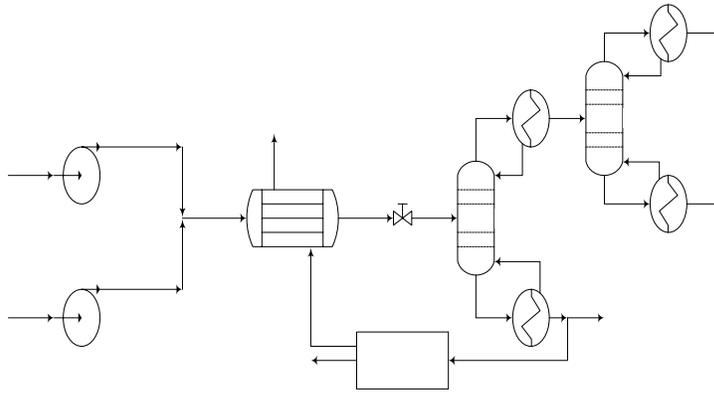
**2.1. Biodiesel production.** Experiments carried out in our laboratory have shown that reacting stoichiometric quantities of methanol or ethanol with soybean oil at 400°C, 100 bar for about three minutes gives nearly complete conversion of the soybean oil to biodiesel (esterified fatty acids). Under these conditions, in contrast to the production of biodiesel under traditional conditions (1 bar, 65 °C, with acid/base catalysts), the reaction rate is 60 times faster, biodiesel is formed using near stoichiometric quantities of alcohol, and very little glycerol is left in the final reaction products. Instead, a number of other compounds are formed resulting from the breakdown of the glycerol. All of these products have not yet been qualitatively and quantitatively identified, but it is expected that many of them can be used directly as part of the biodiesel product. This would simplify the separation process greatly since the glycerol no longer has to be separated from the biodiesel product and additional biodiesel fuel may be produced. In addition, because stoichiometric quantities of alcohol can be used, essentially all of it reacts, eliminating the need for separating it from the biodiesel and recycling it to the TE reactor.

Thus, the process for producing biodiesel from soybean oil becomes quite simple: a reactor with a heat source to produce biodiesel 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, together with water and hydrogen to stoichiometrically balance the esterification reaction. These two products have been identified from the GC/MS analysis of the product stream from the laboratory reactor. The small amount of hydrogen formed is assumed to hydrogenate some of the unsaturated carbon bonds in the linoleic acid esters. The stoichiometric reaction used for the process design is given below.



where: C<sub>6</sub>H<sub>14</sub>O<sub>5</sub> is Diglycerol, C<sub>4</sub>H<sub>8</sub>O<sub>3</sub> is Glycerol Formal, and R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> are hydrocarbon chains of methyl palmitate, methyl linoleate and methyl oleate respectively.

The process flow diagram is shown in Figure 12. The process conditions and the flow rates of each stream in the process flow diagram are given in the appendix in Table A1.



**Figure 12. Process Flow Diagram for Biodiesel Production coupled with Power Generation.**

P-1, P-2: Rotary Positive Displacement Pumps; H-1: Shell and Tube Heat Exchanger; V-1: Pressure Reduction Valve; D-1, D-2: Distillation Columns; C-1, C-2: Condensers; R-1, R-2: Reboilers.

The process consists of pumping the methanol and soybean oil to the esterification reactor at 100 bar, the esterification reactor operating at 400°C, and two distillation columns operating at 1 bar with steam driven reboilers and condensers cooled by cooling water. The first distillation column separates the water and most of the reaction byproducts from the biodiesel (methyl esters). A second column is included in the design to separate the byproducts from the water. The process is unique in that the exhaust from a diesel engine is used to provide heat for the reaction.

The basis for the base-case design was the esterification of 2100 gal/day of soybean oil with 269 gal/day of methanol to produce 2300 gal/day of biodiesel. The plant was assumed to operate 24 hours/day for 346 days a year. The thermodynamic properties of soybean oil, the methyl esters of the three main fatty acid chains of soybean oil (palmitic, linoleic, and oleic) and the assumed byproducts (diglycerol and glycerol formal) were estimated from group contribution methods using CHEMCAD (version 5.5.2) process simulation software from Chemstations. Vapor-liquid equilibrium compositions were estimated by CHEMCAD using the Soave-Redlich-Kwong equation of state (EOS). CHEMCAD was used to design all of the process units except the esterification reactor and diesel engine/ generator set. The reactor was sized based on the residence time used in the laboratory experiments (3 min.) to obtain nearly complete conversion of the soybean oil, although extra volume was allowed to provide sufficient heat transfer area for heating the reaction mixture with the diesel engine exhaust. While designing distillation column D-1, a small percentage of the reaction byproducts was allowed to remain in the bottoms product (biodiesel) since we believe that some byproducts can be included into the biodiesel. The percentage of the byproducts that can be included in the biodiesel fuel is presently unknown and a somewhat arbitrary 1.62 % was included, which possibly could be higher. The remaining byproducts in overheads stream of D-1 were separated from water in D-2. 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. The diesel engine was sized to provide a sufficient amount of heat for the reaction and uses part of the produced biodiesel (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. [G1] and Ulrich [G2]. A list of the major pieces of equipment, their bare module costs in 2006 dollars and the total fixed capital investment (FCI) are given in Table 6.

**Table 6. Capital Costs of equipment.**

Equipment	Capital Costs in dollars ( 2006)
Methanol Feed Pump	32,201
Soybean Oil Feed Pump	61,805
Heat Exchanger/ Reactor	64,763
Distillation Column -1	82,200
Trays for Column -1	5,700
Condenser-1	11,036
Reboiler-1	8,830
Distillation Column- 2	41,550
Trays for Column-2	5,843
Condenser-2	2,650
Reboiler-2	3,975
Diesel Power Generator	75,000
Contingency and Fees	71,200
TOTAL: FCI	466,752

The bare 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 estimated utilities cost, operating labor cost and raw materials cost is given in Tables 7, 8 and 9, respectively. The raw materials costs are for the soybean oil and the methanol. Soybean oil was assumed to be available for \$2.10 /gal [G3] and methanol at \$0.33/gal [G4]. The utilities cost was taken from Turton et al. [G1]. The cost of waste treatment was assumed to be zero.

**Table 7. Utilities Cost.**

Equipment	Utilities	Q (w)	Utilities Usage	Cost in \$/Year ( 2006)
Condensor-1	Cooling Water (30°C)	12,600	4,499,157 Kg/Yr	30
Condensor-2	Cooling Water(30° C)	2,417	3,451,474 Kg/Yr	25
Reboiler-1	Medium Press Steam	35,040	520,327 Kg/Yr	3,803
Reboiler-2	Medium Press Steam	1,309	19,438 Kg/Yr	142
Reactor	Exhaust Gas from Diesel Power Generator	79,357	*	*
Methanol Feed Pump	Electricity from Power Generator	246	2042.7 kWh/Yr	204 <sup>a</sup>
Soybean Oil Feed Pump	Electricity from Power Generator	1,926	15993.5 kWh/Yr	1599 <sup>a</sup>
Total ( C <sub>UL</sub> )	-	-	-	4,000

\* Utilities usage and costs of Exhaust gases were not estimated as it was available from Diesel-Generator;

<sup>a</sup> Electricity costs were not included in Utilities Cost as it was available from Diesel-Generator.

**Table 8. Labor Cost.**

	Operators Per Shift (OPS)	Factor for 24 hr/7 day Week Operation	Annual Operator Salary (AOS)	Total Cost in \$/Yr
$C_{OL}^*$	1.6	4.5	36,000	259,200

\*  $C_{OL} = OPS * \text{Adjusting Factor} * AOS$

**Table 9. Raw Materials Cost.**

Raw Materials	Requirement in Gal/Yr	Costs in Dollars(2006)
Methanol	93,000	30,700
Soybean Oil	770,000	1,489,000
Total ( $C_{RM}$ )	-	1,519,700

COM was calculated from the formula:

$$COM = 0.2860 * FCI + 2.5755 * C_{OL} + 1.16279 * (C_{UT} + C_{WT} + C_{RM}) \quad [G1]$$

The various other items in the COM, such as maintenance costs, supervisory and clerical labor, depreciation of the FCI, and administration, distribution and selling 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 10, together with revenue from the sale of electricity, and the break-even cost of the net biodiesel fuel available for sale.

**Table 10- Comparison of Cost of Biodiesel for Three Process Options**

OPTION	Biodiesel Capacity ( Gal/ Day)	COM \$/Yr	Electricity Revenue \$/Yr	Biodiesel 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 Diesel 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 biodiesel, COM was estimated to be \$ 2,572,804/ yr. The total electricity produced from power generator is 1,171,196 kWh/yr, but 18,036 kWh/yr are used to drive the methanol and soybean

oil feed pumps, leaving 1,153,160 kWh/yr available for sale. Assuming that the selling price of electricity to commercial or industrial sector 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 Biodiesel produced per year is 800,557 gal/yr. 11.4 % of the total is used for generation of electricity by the diesel-generator; hence the remaining 88.6 % of Biodiesel available for sale is 709,774 gal/yr. The break even cost of biodiesel per gallon is  $(\$2,457,488/\text{yr}) / 709,774 \text{ (gal/yr)}$  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 biodiesel product of \$2.95/gal, \$ 2.68/gal, \$2.61/gal, and \$2.56/gal respectively.

A second alternative design that was considered was the use of a direct-fired Dowtherm heater fueled by the biodiesel products to heat the esterification reactor instead of exhaust from the diesel generator. This option reduces the biodiesel fuel needed for heating the reactants to only 3.0 % of the biodiesel product, substantially reducing the cost of the biodiesel. For a process producing 9200 gal/day of biodiesel, 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 biodiesel 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 biodiesel fuel increases by 16.5 % and only a single distillation column is required. For producing 9200 gal/day of biodiesel using this option, its cost is reduced to \$2.49/gal. This would be extremely competitive with the current price of diesel fuel of ~\$2.60/gal. [G5]

## **2.2. Soybean oil extraction.**

We are currently working on the optimized design and economics of SC-CO<sub>2</sub> extraction of soybean oil. Currently, the work is in progress and the details about the process conditions and the economics would be provided in future. The process flowsheet for SC-CO<sub>2</sub> extraction of soybean oil is shown in Figure 13.



**Section 3**  
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## **APPENDIX**

**Table A1. Process Stream Conditions for Biodiesel Production coupled with Power Generation Process Flow Diagram**

Stream No.	1	2	3	4	5	6	7	8	9	10	11	12	13
Temp (° C)	25	25	30	30	30	400	400	96	296	296	296	143	99
Press (bar)	1	1	100	100	100	100	1	1	1	1	1	1	1
Flowrates in gmol/min													
Soybean oil	5.8	0.0	5.8	0.0	5.8	0.03	0.03	0.0	0.03	0.0	0.03	0.0	0.0
Methanol	0.0	17.4	0.0	17.4	17.4	0.1	0.1	0.1	0.0	0.0	0.0	0.09	0.01
Methyl Palmitate	0.0	0.0	0.0	0.0	0.0	2.23	2.3	0.0	2.3	0.41	1.89	0.0	0.0
Methyl Oleate	0.0	0.0	0.0	0.0	0.0	5.16	5.16	0.0	5.16	0.92	4.24	0.0	0.0
Methyl Linoleate	0.0	0.0	0.0	0.0	0.0	9.87	9.87	0.0	9.87	1.76	8.11	0.0	0.0
Glycerol Formal	0.0	0.0	0.0	0.0	0.0	1.73	1.73	1.44	0.29	0.05	0.24	0.0	1.44
Diglycerol	0.0	0.0	0.0	0.0	0.0	1.73	1.73	1.47	0.26	0.05	0.21	0.0	1.47
Water	0.0	0.0	0.0	0.0	0.0	3.46	3.46	3.46	0.0	0.0	0.0	3.46	0.0
Total(gmol/min)	5.8	17.4	5.8	17.4	23.2	24.31	24.31	6.47	17.91	3.19	14.72	3.55	2.92
Total (gal/day)	2092	269	-	-	-	-	-	-	2313	416	1897	-	-