A Portable, Automated and Environmentally Friendly Biodiesel Processing System

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ABSTRACT

The relatively recent developments in heterogeneous-catalyst based supercritical biodiesel processing have enabled the construction of a simple, portable, efficient, automated and environmentally friendly biodiesel processing system. The processing of biodiesel in the supercritical state uses no water, produces negligible waste and is insensitive to the free-fatty acid content in a lipid.

In this paper an overview of the supercritical transesterification process as it applies to the design of a portable biodiesel processing system will be discussed. In addition, the details of the design and performance of a first-generation prototype biodiesel processing system are described.

INTRODUCTION

Peak oil production is predicted to occur in 2014 [1]. As the petroleum resources of the planet are stressed, the importance of utilizing available lipids as a biofuel replacement for petroleum-based-fuels will increase. The advantages of biodiesel (FAME; Fatty Acid Methyl Esters) as a substitute for petrel-diesel have been extensively documented in both the technical and popular literature [2-4, 5]. Several technologies exist for producing FAME that most commonly utilize the transesterification reaction with an alkaline catalyst [6, 7]. Since the major percentage of the final price of biodiesel is controlled by the price of the raw material, it is beneficial to use inexpensive sources such as grease and tallow [8]. It is also highly desirable to use non-food based lipid sources in order to avoid competition between fuel, food and land [9]. Unfortunately inexpensive lipid sources often contain high levels of free fatty acids (FFA) which via the competing saponification reaction can produce soap in addition to biodiesel. The preprocessing necessary to reduce FFA to acceptable levels along with the post-processing removal of end products such as residual saponified reactants, glycerol and catalyst increase the cost of the biodiesel and require the use of large amounts of water [10, 11]. The many advantages of processing lipids into biodiesel in the supercritical state have been previously discussed [12-17].

Processing lipids and alcohol in the supercritical state to produce biodiesel started receiving significant attention circa 2000. The first demonstration of the transesterification of vegetable oil

in supercritical methanol without a catalyst was published by Saka et. al. and Kusidianna et. al. in 2001 [18, 19]. Their work demonstrated that biodiesel produced in the supercritical state was equivalent to biodiesel produced by traditional base-catalyzed methods. In their work, the reaction time and the amount of glycerin produced were also reduced when compared to biodiesel produced by traditional base-catalyzed methods. The conversion of rapeseed oil with a 42:1 molar ratio of methanol to lipid was reported to be 90%. Reaction times as low as 240 seconds at 350°C were also noted. Transesterification was carried out in a batch process where pressures were monitored but not controlled. Reactor pressures in the 34.5 – 62 MPa range were noted.

The work of Saka et. al. and Kusidianna et. al. was followed by others [20-29]. The list is intended to be representative of the large amount of literature published on supercritical state processing of biodiesel during the past decade. An additional compilation of conversion efficiencies with references can also be found in Table 1 of [30]. In all cases, the un-catalyzed supercritical transesterification reaction time for converting a wide variety of vegetable oils with methanol to biodiesel was reduced when compared to typical base-catalyzed methods. The production of glycerin, compared to traditional base-catalyzed biodiesel production methods, was also reduced [31]. Representative results are summarized in Table 1. For reference, the critical point of methanol is ~ 240°C and 8.09 MPa.

Author	Publication Year	Lipid	MeOH:Lipid Molar Ratio	Processing Temperature (°C)	Processing Pressure (MPa)	Reaction Time (s)	Biodiesel % Yield
Saka et. al. [18]	2001	Rapeseed	42 - 1	350	43	240	~ 98
Kusdianna et. al. [19]	2001	Rapeseed	42 - 1	250 - 375	35 - 65	240	~ 90
Demirbas et. al. [20]	2002	Rapeseed	41 - 1	250	8.1	300	~ 95
Madras et. al. [21]	2004	Sunflower	40 - 1	400	20	2400	98
Van Ginneken et. al. [22]	2005	Rapeseed	25 - 1	300 - 325	12	900	> 98
			41 - 1	300 - 325	12	300	> 98
Rathore [23]	2006	Sunflower	40 - 1	350 or 400	20	1800	95 - 98
Bunyakiat et. al. [24]	2006	Palm, Coconut	42 - 1	350	19	400	96
Schulte [25]	2007	Chicken Fat	40 - 1	325	11.4	1200	~ 90
He et. al. [26]	2007	Soybean	40 - 1	300	40	1500	~ 80
				100 - 300 ramp			~ 96
Valle et. al. [27]	2008	Rapeseed	39 - 1	300 - 325	10 - 15	720	97.5
McNeff et. al. [28]	2008	Multiple	32 - 1	325 - 375	15 - 25	< 60	> 90
Hong [29]	2009	Palm	60 - 1	325	35	2400	~ 80
			20 - 1	325	35	2400	~ 85

Table 1. Survey of supercritical processing of lipids and methanol

In 2008, a description of a supercritical biodiesel processing utilizing a heterogeneous catalyst was set forth [28]. That supercritical process used a fixed-bed continuous-flow reactor containing a metal-oxide based catalyst. Similar to previously reported works, this process does not require the use of water and produced a negligible amount of waste. Operating temperature and pressure ranges were reported as 300°C – 400°C and 17 – 28 MPa, respectively. Furthermore, the simultaneous transesterification of triglycerides and esterification of FFAs with short reaction

times on the order of a few seconds was also reported. The reported conversion of the source lipid to biodiesel in an excess of alcohol was greater than 90% (see Table 1 and [30]). The final output may require post-processing absorption of excess FFAs or additional esterification of the FFAs with a suitable fixed-bed heterogeneous catalyst [31]. The moderate temperature and pressure operating conditions, combined with a short reaction time and continuous-flow through a fixed-bed heterogeneous catalyst make this type of supercritical process suitable for use in a portable biodiesel processing system.

The preliminary design of any system is aided with the knowledge of key material properties such as heat capacity and density as functions of temperature and pressure. During the design and test phases associated with the development of the portable biodiesel equipment described in the next section, public domain information on the material properties of supercritical methanol with any lipid were found to be incomplete. Hence, the first generation portable equipment was conservatively designed to account for these uncertainties in order to explore biodiesel processing in the supercritical state.

After the development of the first generation portable biodiesel equipment described in the next section, Chen et. al. [32] reported extensively on the material properties of methanol in the supercritical state. However, the supercritical state properties of the lipid-plus-methanol system are still not well known or documented in the public domain. Since portable biodiesel equipment of the type described in this paper has the potential of being used with a wide variety of lipids, building flexibility into the system was important in order to study the processing characteristics of a wide variety of lipids and process operating conditions (e.g. temperature, pressure, flow rate and catalyst).

With the proper operating conditions and heterogeneous catalyst, supercritical state processing has been found capable of transforming a lipid (plant oil or animal fat) with a molar-excess of alcohol (typically methanol) into biodiesel with only residual organics, FFAs and unreacted alcohol. The unreacted alcohol and near-ASTM grade biodiesel readily separate after supercritical state conversion and subsequent return to STP conditions. While the supercritical state process could be operated in a batch mode, the process allows for a continuous flow operation. A block-diagram illustrating the processing equipment is shown in Figure 1.

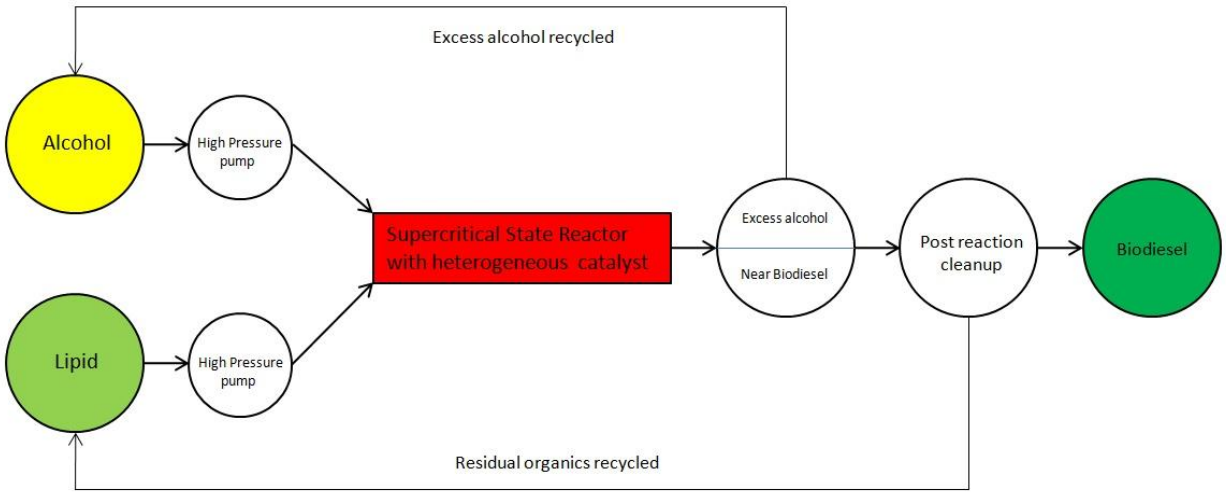

Figure 1. Flow schematic of the new process

The biodiesel reaction occurs in the reactor under supercritical conditions which for many lipid-methanol combinations requires modest temperatures and pressures on the order of 325°C and 21 MPa respectively. The reaction can be catalyzed with a heterogeneous catalyst such as porous zirconia, titania or alumina [28]. The catalyst is not consumed in the reaction. Depending on operating and flow conditions, the reactor can be sized to produce various percentage combinations of near-biodiesel, excess methanol and FFAs. The FFAs can be removed in a post-process cleaning operation and returned to the input lipid stream [31]. The general characteristics of a supercritical catalyzed process are contrasted with those of a state-of-the-art conventional biodiesel process and summarized in Table 2.

PROCESSING CHARACTERISTICS	PROCESS COMPARISON	
	Traditional Biodiesel Processing	Supercritical State Biodiesel Processing
Uses water	Yes	No
Sensitive to water	Yes	No
Waste by-products	Yes	No
Possibility of soap production	Yes	No
Sensitive to FFAs	Yes	No
Processing	Batch or Flow	Batch or Flow
Use of catalyst	Homogenous	Heterogeneous
Catalyst cleaning	Yes	No
Reaction rate	Minutes to Hours	Seconds to Minutes
FFA conversion to biodiesel	No	Yes
Glycerol output?	Yes	Residual

Table 2. Comparison of a traditional biodiesel process and the new process

Supercritical state processing of lipids and alcohol to produce biodiesel has been successfully tested on a wide variety of lipids (plant oil or animal fat) that include lipids such as acidulated soap stock, soybean oil, sunflower oil and algae oil [see Table 1 references]. The portable biodiesel equipment discussed in the following sections is capable of processing most of these lipids into biodiesel.

THE PORTABLE BIODIESEL PROCESSING SYSTEM

The system

A photograph of the first generation portable biodiesel processing system is presented in Figure 2 with details summarized in Figure 3. The processing unit has three separate subassemblies which are joined prior to operation. Quick-disconnect fluid and electrical connectors link the sections and enable rapid assembly and disassembly. The subassemblies, from the left-to-right in Figure 2, are referred to as the *input*, the *refinery* and the *output* assemblies. Individual assemblies have casters and can be easily transported. A functional description of each section is summarized in Figure 3. The heaviest section is the central refinery section which has a mass on the order of 180 kilograms. The empty mass of each of the other two sections is approximately 36 kilograms. For transportation the entire system is sized to fit onto the bed of a standard pickup truck. Aggregately, the biodiesel processing system shown in Figure 2 is referred to as "Gen1" (first generation) and is capable of producing up to 76 kiloliters of biodiesel per year.

Figure 2. The portable biodiesel processing unit based on the new process

Left Section: Input	Center Section: Refinery	Right Section: Output
Low temperature and pressure	At processing temperature and pressure	Low temperature and pressure
• Input Tanks • Insulated lipid tank • MeOH tank • Low pressure feed pumps (bottom) • Sparging unit • Quick assembly connectors • Casters for transportation	• Control electronics • Pressure pumps • Back pressure regulator • Sensors • Heat exchanger • Pre-heater • Reactor • Quick assembly connectors • Casters for transportation	• Separation weir • Separation plumbing • MeOH recycling tank • Biodiesel output tank • Overflow tank • Quick assembly connectors • Casters for transportation

Figure 3. Description of the portable-biodiesel-processing-unit sections shown in Figure 2

The design objectives of the system were:

i. Demonstration of a portable processing unit using supercritical state processes
ii. Assessment of the robustness of supercritical state processing
iii. Assessment of the economics associated with a portable supercritical state processing system
iv. Assessment of the required controls and operating conditions
v. Identification and development of suppliers, documents and materials.

As previously noted, many of the material properties of the lipids-plus-methanol mixture in the supercritical state were unknown. In addition, the processing robustness (defined as the percent variation in the quality of the produced biodiesel) as a function of processing-parameter-variation, was unknown. Hence it was necessary to develop a test-bed that enabled assessment of the indicated design goals. The Gen1 system succeeded in meeting all of the design goals and produced near ASTM grade biodiesel very early in the development design cycle.

Samples of the output of the system from several trial runs are shown in Figure 4. Excess methanol was removed prior to collecting these samples. Processing factors such as temperature, pressure and the effect of nitrogen sparging (for removing dissolved oxygen in the input streams) contributed to the observed color in each of the samples. The darkest colored sample was processed at higher temperatures (e.g. near 400°C) without sparging. Analysis suggests that the residual oxygen oxidized some of the organics in the flow with the resulting dark colors.

Figure 4. Output samples from the portable biodiesel system

An assay summary of one of the samples is illustrated in Table 3 [33]. This particular run produced near ASTM grade biodiesel with the exception of acid number. Reduction of the acid number may require additional post processing as previously noted. The as-processed glycerol levels were below ASTM levels for biodiesel.

Analysis	Level Found	Status	ASTM 6751 Limits	Method	Analysis Date
Oxidation Stability (hrs)	n/a-volatile	Pass	3 min	EN 14112	04/28/09
Flash Point (deg C)	below 4	Pass	93 min	ASTM D93-07	04/28/09
Acid Number (mg KOH/g)	13.3	Fail	0.50 max	ASTM D664-07	04/28/09
Free Glycerine (% mass)	< 0.001	Pass	0.020 max	ASTM D6584-07	04/28/09
Totoal Glycerine (% mass)	0.13	Pass	0.240 max	ASTM D6584-07	04/28/09
Monoglyceride (% mass)	0.011			ASTM D6584-07	04/28/09
Diglycerides (% mass)	0.007			ASTM D6584-07	04/28/09
Triglycerides (% mass)	0.112			ASTM D6584-07	04/28/09
Cold Soak Filtrationn	less than	NA	360 sec. max	ASTM D7501	04/28/09

Table 3. Independent laboratory analysis results

Design and Subsystems

The subsystems of the portable biodiesel unit are summarized in Table 4. The design of the fluid and thermal subsystems of the portable biodiesel system are determined by first establishing the annual biodiesel production volume (liter per year – lpy) and the number of operating hours per year. These parameters in turn are used to define several system parameters such as flow rate, the sizing of the high-pressure-pumps and associated equipment, the tubing and connectors needed to handle the flow and pressures and temperatures. Finally, an efficient thermal subsystem is essential for overall energy efficiency. The flow rate also controls the size of the reactor as fluid latency in the reactor ultimately determines the conversion efficiency from the initial supercritical mixture of methanol-plus-lipid to biodiesel. Depending on the conversion efficiency, post-processing may be necessary. The Gen1 reactor was over sized to produce near-biodiesel in order to minimize post-processing requirements with the further objective of

eliminating all post-processing other than the trivial methanol-biodiesel separation step. Finally, the annual volume target and flow rate also affects the sizing of the input tanks, the output tanks and the weir wherein the biodiesel-methanol mixture separates upon return from the supercritical state to STP conditions.

Subsystem	Components
Fluid	pumps, tubing, fittings, connectors
Thermal	heat exchanger, preheater, insulation
Reaction	reactor, catalyst
Control	microprocessors, sensors, communication links
Power	distribution, safety
Tanks	input, output weir
Structure	frame, casters, skins

Table 4. Summary of the subsystems in the portable unit

The experimentally observed volumetric reaction for an efficient supercritical process with a 33:1 molar ratio of methanol (MeOH)-to-lipid was found to be [10, Table 3]

(1 L lipid) + (1.32 L MeOH) → (1.38 L biodiesel) + (1.2 L MeOH excess) + (residuals). (1)

The high-conversion efficiency and reduction of glycerin observed in the supercritical state processing of biodiesel results in a slight increase in the amount of biodiesel produced when compared to that of a traditional base-catalyzed biodiesel process. These reaction volumes combined with flow rate specifications are used to size the input tanks, the output tanks and the weir.

The design specifications for the Gen1 system are summarized in Table 5. These specifications target two applications. The first is for humanitarian-based power applications in developing countries where sustainable biodiesel would replace expensive petrel-diesel. The second application is based on the diesel-fuel demands for farms on the order of 600 – 800 ha (1500 – 2000 acres). Farm of this size are common in North America. The specifications in Table 5 satisfy both applications. Methods for obtaining lipids and alcohols, extracting and filtering the lipid, training users and generating electrical power from the biodiesel will be addressed in a future publication.

15,000 liters per year ASTM grade biodiesel
200 days per year operation
6 hour per day operation
Processing temperature: 300 - 400°C
Processing pressure: 13 - 40 Mpa
The system is transportable in a standard pickup truck

Table 5. Summary of design specifications

Flow and Thermal Layout

The sizing of the refinery components is largely dictated by the desired flow rate along with the thermal layout. The flow rate determines the size of the reactor, the size of the pumps (and associated cost of the pumps) and affects the design of the thermal subsystem. The thermal layout directly affects the processing input-energy associated with the system and the design of the heat exchangers. The energy factor η of the system is defined as the ratio of energy that can be obtained from the produced biodiesel to the energy required to make the biodiesel fuel. In a small system, it is essential to maximize η. This is particularly critical for humanitarian applications where the energy factor must be optimized and costs minimized. Analysis of Gen1 operating data suggests that a small biodiesel system of the type being described can achieve an η on the order of 3 – 4.

The thermal design of the system is shown in Figure 5. The details of the thermal layout are most simply described when fluid flow through the reactor is used as the descriptive starting point. The thermal energy and density of the fluid is greatest in the reactor due to the supercritical operating conditions. The output flow of the reactor enters a very efficient counter flowing type of heat-exchanger where liquid-to-liquid heat transfer preheats the relatively cold input stream consisting of pressurized lipid-plus-methanol. The preheater, located upstream of the reactor, raises the final temperature of the flow to the desired reactor operating temperature. The pressure of the flow between the high-pressure-pumps and the back-pressure-regulator exceeds the critical pressure of the lipid-plus-methanol mixture. Therefore the temperature and pressure of the flow at the head of the reactor determines the reaction operating conditions of the supercritical lipid-methanol state. The heterogeneously catalyzed process occurs in the reactor. After the flow passes through the back-pressure-regulator the remaining residual heat is used to warm the lipid input tank. Careful design of the physical layout of the thermal sub-system and insulation of the thermal subsystem maximizes overall thermal efficiency.

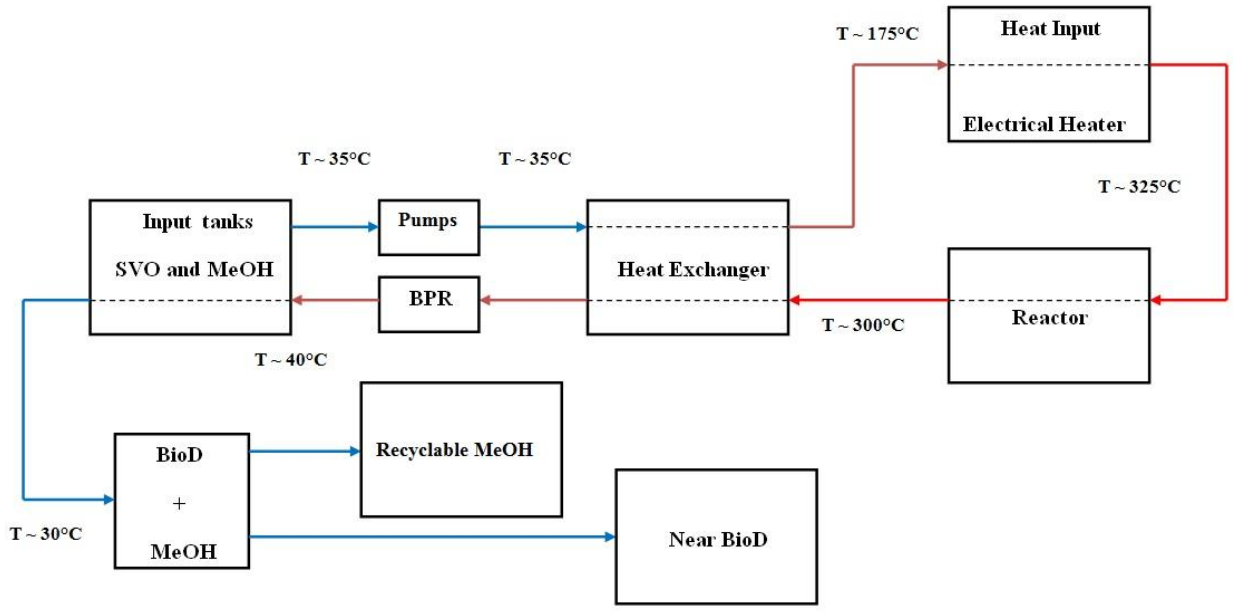

Figure 5. Flow diagram of the thermal subsystem. Blue lines represent relatively cool fluid-flow while red lines are representative of hot fluid-flow.

Based on user requirements, the system is capable of producing approximately15,000 liters of biodiesel per year (lpy) during 1200 operating hours. This corresponds to a flow rate of 210 mL per minute (0.0555 gpm). As noted in the Introduction, due to an absence of material properties in the supercritical state, the pumps and electrical heaters, in concert with equation 1, were over-specified in order to guarantee achieving supercritical-state operation. Using the calculated flow and an estimated heat-capacity for the lipid-plus-methanol [2554 J/(kg-°C)], the preheater is capable of heating a fluid with ten-times the estimated heat capacity of the flow (lipid-plus-methanol) at a flow-rate of ten-times that required for achieving 15 kLpy. For nominal flow conditions, the heat exchanger was designed for an inlet-outlet temperature difference of 200°C. The input tanks, the output tanks and the weir were sized for a six-hour operating period (~ 76 liter capacity) which corresponds to a single day of operation.

Reactor and materials, Control and Electrical subsystems

The reactor incorporated zirconia particles and was sized for a fluid latency of 60 seconds at the 210 mL per minute nominal flow rate. This latency is an order-of-magnitude greater than the reported conversion rates in [28] consistent with the order-of-magnitude overdesign of the pumps and thermal subsystems. Stainless steel tubing and fittings were used in the entire fluid path wherever the temperature or pressure of the working fluids exceeded ambient conditions. For user safety the entire system was leak checked at 25% higher pressures than the highest operating pressure (5000 psi) and temperature (400°C).

The block diagram of the control system is illustrated in Figure 6. The control system consisted of a PLC with appropriate I/O modules, touch-panel user interface, multiple sensors, control relays, Variable-Frequency-Drives (VFD) for controlling the induction motors that run the pressure pumps and control wiring. The power distribution system consisted of two 208 VAC three-phase 30-A supplies which were used to power the overall system. Power control relays were used for safety and could be controlled by the operator or the PLC. The entire electrical system and grounding was certified by a qualified electrician prior to operation. The PLC performs logic handling, controls the user interface and the various processing I/O operations. The various sensors – which include flow sensors, pressure, temperature and vacuum sensors – as well as all logic-level-status-signals are read by the PLC which executes code and makes decisions to control the output based on user inputs from the touch panel or the remote wireless Ethernet connection. An E-stop feature is used to shut down the system either manually or via the PLC in the event of an emergency.

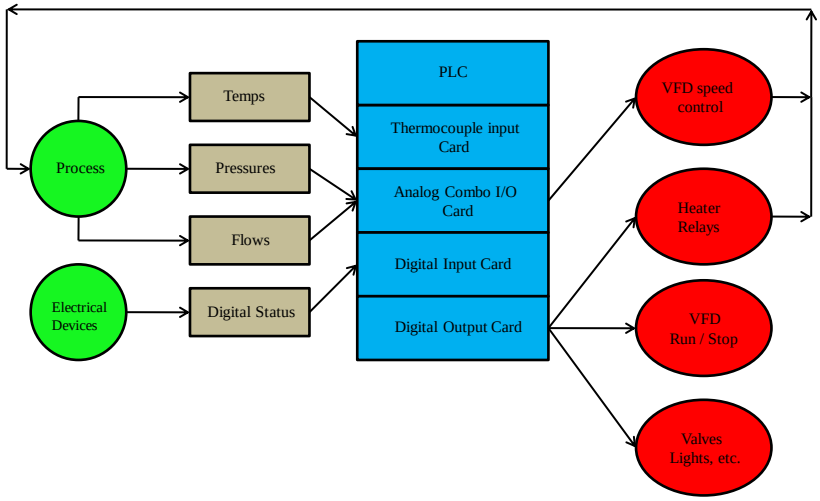

Figure 6. The control system

Subsystem Characteristics

The subsystem and component requirements of the portable biodiesel system shown in Figure 2 have several unique characteristics. First, even though the temperature range (300 - 400°C), the pressure range (13 - 40 MPa) and flow-rate range (100 - 300 mL per minute) for the supercritical processing of biodiesel fuel are not extreme, these parameter ranges tend to fall just outside of

the ranges addressed by low-end oil petroleum-processing equipment. This type of equipment, which must be very robust for reliably handling the harsh conditions found in the oil industry, has a correspondingly high cost. Furthermore, the operating temperature and pressure necessary for supercritical state processing, combined with the fluid characteristics (e.g. FFA levels), requires the use of stainless steel components throughout the high-pressure portions of the system. This includes tubing, the reactor, the heat-exchanger, the preheater, the pumps and all sensors. Since the cost of stainless steel can be prohibitive, additional attention to economics is essential for containing costs.

Another unique challenge for the system was that pumps capable of developing pressures in the 13 – 40 MPa range for flow-rates consistent with producing biodiesel fuel in the 15 – 38 kLpy range were not available. For these pressures, multiple suppliers had acceptable pumps for flow-rates in the $\geq$ 4 lpm range or $\leq$ 0.04 lpm range. The pressure pumps that were ultimately selected for use were higher flow units that were speed-reduced with a 3:1 gear box to slow the flow while maintaining pressure. The economics associated with these pumps will need to be addressed in future system design work. While non-trivial, the design, engineering and implementation details for the remainder of the system were typical.

DISCUSSION

The engineering details and construction of the portable biodiesel processing system turned out to be remarkably straightforward after the flow-rate, operating pressure and temperature were specified. Processing in the supercritical state was experimentally found to be reproducible, robust and yield-tolerant over a relatively wide range of operating conditions and lipids. Near ASTM grade biodiesel was processed during the initial trials and routinely processed after optimized operating conditions were determined. Process control simply required specifying the operating flow-rate, temperature and pressure. The experimentally observed processing characteristics combined with the straight-forward construction details are expected to result in a significant system simplification in follow-on units. The cost of materials for the next generation optimized system is projected to be less than $20,000 U.S. based on system studies. The size and weight of the refinery section (central section, Figure 2) can be reduced to approximately half of that of the Gen1 unit. An energy analysis based on Gen1 data suggests that it is possible to achieve a 3-to-1 energy factor where the energy of 1 unit of produced biodiesel fuel would produce up to 4 units of biodiesel fuel.

The intended users of the follow-on equipment are expected to be humanitarian groups and individuals. This includes non-profit groups, farmers, small business owners, universities, and single users. For the most part, the intended users are not expected to have engineering, chemical or technician skills or access to engineering resources. This requires that attention be paid to system reliability, robustness, operating simplicity and economics. These principles guided the

entire design and selection process for all components and suppliers. Collaborative work with component vendors and their application engineers facilitated achieving overall system robustness and reliability. Since direct operating experience has demonstrated that the process is remarkably reliable and robust with significant processing latitude (with respect to 'key processing input variable' variances) for a wide variety of input lipids, it is anticipated that when follow-on systems are constructed which incorporate the Gen1 experiences, that they will meet the needs of the intended users.

SUMMARY

A portable biodiesel processing system using supercritical state processing of methanol and lipids has been successfully designed, built and tested. Near ASTM grad biodiesel was made on the initial trial runs. The system does not require the use of water and produces negligible waste. After supercritical processing, when the processed fluid returns to atmospheric pressure and room temperature, the output stream naturally separates into methanol and biodiesel. After post-processing the methanol is recycled and the biodiesel is ready for use. The successful operation of the portable system lays the foundational work for developing a truly portable, simple and automated biodiesel production system that is largely insensitive to the input lipid feedstock. The follow-on units will have significant humanitarian and single-user applications.

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