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## HIGH SHEAR MIXING REACTOR FOR GLYCEROLYSIS

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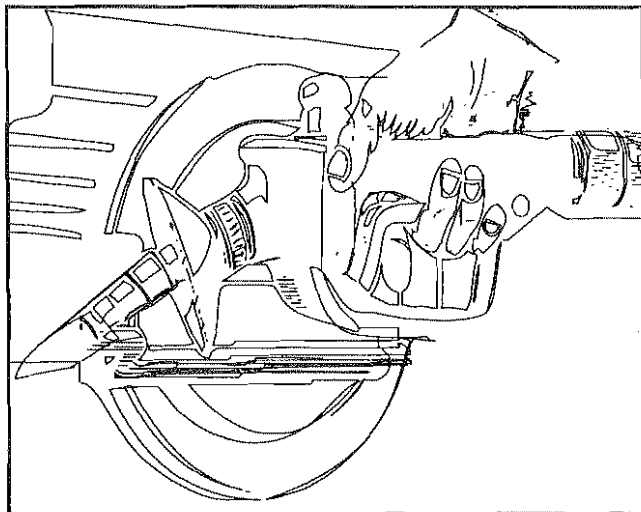
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# Liquid Fuels, Lubricants and Additives from Biomass



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# HIGH SHEAR MIXING REACTOR FOR GLYCEROLYSIS

Hossein Nouredini<sup>1</sup>

## ABSTRACT

Increased environmental awareness and depletion of resources are driving industry to develop alternative fuels from renewable resources that are environmentally more acceptable. Esters of fatty acids (bio-diesel), derived from the transesterification of vegetable oils, have properties similar to components of petroleum based diesel fuel. Cost has been a major factor slowing the commercialization of biodiesel. In order to improve the economy of this process two factors were investigated in this study: 1) use of beef tallow as raw material and 2) by-product utilization.

Glycerol is the by-product of the esterification process. In this work the feasibility of the glycerolysis of vegetable oils with crude glycerol, from the transesterification of vegetable oils and animal fats, in a continuous high shear mixing reactor has been studied. The preliminary investigations indicates the potential for a higher yield of monoglycerides at more moderate temperatures than traditional processing.

Transesterification of beef tallow produces a mixture of esters which is more concentrated in the saturated fatty acids. Physical properties of these esters are similar to esters of vegetable oils. Reaction results and properties for esters of beef tallow are presented.

**Keywords:** Triglycerides, Glycerol, High shear reactor.

## INTRODUCTION

Increased environmental concerns, tougher Clean Air Act standards, and depletion of raw material (petroleum feedstock) are driving industry to come up with viable alternative fuels that burn more cleanly, a field in which vegetable oils and animal fats may play a major role. Limited use of fuel from vegetable oils is hardly new. Vegetable oils have been considered as fuel for diesel engines since the earliest days of the compression-ignition engines. Rudolph Diesel, the inventor of the compression-ignition engines, used peanut oil in a 1900 demonstration. While short term tests are almost always positive (e.g., Mazel et al., 1985; Samson et al., 1985), long term use of neat vegetable oils leads to severe engine problems such as deposition, ring sticking, and injector coking (Peterson et al., 1983). High viscosity and a tendency for polymerization within the cylinder appears to be at the root

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of many problems associated with direct use of these oils as fuels (Ryan III et al., 1984; Peterson, 1986).

Fatty esters (biodiesel) from vegetable oils and animal fats have shown promise as alternative diesel fuels as a result of improved viscosity and volatility relative to the triglyceride (Clark et al., 1984). This has stimulated interest in optimization of transesterification reaction conditions. The esterification process involves the transformation of the large, branched, triglyceride molecules of bio-oils and fats into smaller, straight-chain molecules, similar in size to components of diesel fuel. An insoluble phase, rich in glycerol is the by-product of this process. The transesterification process (also called alcoholysis) has been intensively patented as widening industrial uses were found for esters (e.g., Tanaka et al., 1981; Sankaran, 1990; Meffert, 1984; Freedman et al., 1984).

The chemical and physical properties of biodiesel closely resemble those of diesel fuel. This has been documented by many workers (e.g., Clark et al., 1984; Mittelbach et al., 1988). Biodiesel's cetane number, energy content, viscosity and phase changes are similar to petroleum-based diesel fuel. In addition, biodiesel is essentially sulfur free. Engines fueled by biodiesel emit significantly fewer particulates, hydrocarbons, and less carbon monoxide than those operating on conventional diesel fuel. Emissions of  $NO_x$  however are similar to those of diesel engines operating on conventional diesel fuels (Mittelbach et al., 1988).

Biodiesel also offers enhanced safety characteristics when compared to diesel fuel. It has a higher flash point and does not produce explosive air/fuel vapors. Moreover, it is biodegradable, less toxic, and, compared to petroleum fuel, biodiesel emissions from an engine operating on these fuels are less toxic due to an absence of aromatic hydrocarbons. The esterified vegetable oils have a higher cloud point than diesel fuels and require engine and fuel heaters when used as a pure fuel in climates where the temperature dips below 30°F. However if the esterified oil is blended with regular diesel fuel, no heater is required.

While biodiesel fuels have been around since World War II, their high cost has been a major obstacle for commercialization. Their current role in the market place is largely tied to environmental concerns and the more stringent government standards. This may change if the crude glycerol by-product from the transesterification process is utilized for production of derivatives of glycerol such as mono- and diglycerides. Glycerolysis of vegetable oils or animal fats produces a mixture of mono- and diglycerides which are valuable chemical intermediates. The conventional glycerolysis process has been investigated and patented by many workers (e.g., Rheineck et al., 1968; Sonntag, 1982; Alsop et al., 1963; Birmann 1959 and

In this study the feasibility of the use of a high shear mixing device for dispersion of immiscible liquid phases and achieving the contact requirements for transesterification and glycerolysis processes has been studied. Reaction results for the transesterification of beef tallow are also presented.

### Experimental

Transesterification of Triglycerides Although the transesterification of vegetable oils or animal fats can be done in an unsophisticated process, the process conditions must be carefully controlled and/or modified to achieve maximum yield (98+) at the lowest temperature and reaction time. In the conventional transesterification reaction the reactor is initially charged with oil or fat, methyl alcohol in an amount of 2 to 10 equivalents, and sodium hydroxide catalyst in an amount of 1 to 1.0% by weight based on the fatty acid glycerides. The reaction mixture is then heated to the boiling temperature of methyl alcohol and refluxed for about an hour under agitation. A conversion of 90 to 99% is usually obtained to form a blend of fatty esters. With the agitation stopped, the reaction mixture will separate into an upper layer of transesterification product and a lower layer of glycerol diluted with unreacted methyl alcohol. The fatty ester product in the upper layer should be further neutralized and vacuum distilled for removal of excess alcohol before use as fuel.

Experimental investigations for the transesterification of beef tallow in a batch reactor reveal that a 98% conversion of triglycerides to fatty esters can be achieved in one stage using 0.12% catalyst after one hour of reaction time. Results are tabulated in Table 1, based on high pressure liquid chromatography analysis. Unlike vegetable oils, beef tallow's transesterification tends to form a gel-like material in some experimental runs. High concentration of saturated fatty acid components in beef tallow, poor agitation, and low conversion of triglycerides are suspects for this phenomena. Incomplete reactions and/or reverse reactions result in formation of mono- di- and even triglycerides with relatively high melting points. These will simply form a solid or gel-like phase.

The degree of homogeneity (emulsification) of alcohol in the triglyceride phase is of great importance in the transesterification process. In conventional alcoholysis these factors are induced through mechanical mixing and increasing the temperature of the reactor. Because of its high melting point and higher viscosity, this effect is particularly important to the transesterification of tallow. Preliminary results suggest that a high shear mixing device is capable of providing the liquid-liquid contact necessary for high conversion at a relatively short residence time.

One of the most important factors in the glycerolysis process is the solubility or the degree of contact between the triglycerides and glycerol. The catalyst used in glycerolysis reacts with triglycerides to form soap, which promotes the reaction, at least in part, acting as an emulsifier for glycerol in the fat or oil phase. Similarly, the increase in the temperature aids in the mass transfer of the triglyceride to the glycerol phase and to a faster rate of reaction by increasing the mutual solubility of the fat and glycerol phases. Due to the decomposition of some fatty acids at

recovered while unreacted starting materials are recycled back into the reaction vessel. Through conventional purification steps a mixture of mono-, di- and triglycerides, reaction mixture is rapidly cooled to minimize the reversion of the monoglycerides, tried to a maximum of 250°C and the reaction is completed in 15 minutes. The reactor with an inert gas such as nitrogen. The reaction temperature is carried from oxidation. The reactants are further protected from oxidation by blanketing charge is rapidly heated under reduced pressure, to remove air, and to protected kaline catalyst, preferably anhydrous sodium or potassium hydroxide. Then, the triglycerides, about 25-40% of its weight of glycerol, and 0.05-0.20% of an al- In the conventional glycerolysis reaction, the reactor is initially charged with glycerolysis. Glycerolysis is the transesterification of glycerol with triglycerides.

<sup>a</sup> Soybean oil. All others are beef tallow.

Run #	% Catalyst	Reaction Time (hrs)	No. of Stages	%yield
320592	.3 <sup>a</sup>	1.5	2	75.0
040292	1.35 <sup>a</sup>	1.5	2	78.5
051192	1.0 <sup>a</sup>	2.0	1	80.0
061892	.75	1.5	2	83.1
061992	1.40 <sup>a</sup>	1.5	2	74.6
062392	2.05 <sup>a</sup>	1.5	2	73.9
062592	1.0	2.0	2	81.4
062992	.75	1.5	1	71.4
063092	.50	1.5	1	85.9
070292	.53	1.5	1	97.0
070392	.42	1.5	1	98.0
070492	.33	1.5	1	95.0
070692	.52	1.0	1	96.2
170692	.50	2.2	1	95.8
070792	.61	1.5	1	90.5
072292 <sup>b</sup>	.41	1.0	1	98.0

<sup>a</sup> 50% NaOH solution. All others are solid NaOH.

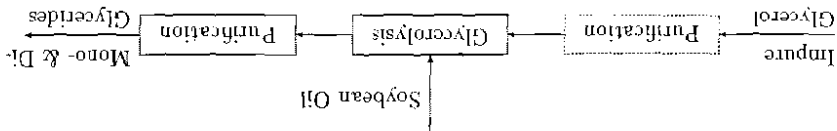
Table 1: Transesterification Reaction Results.

high temperatures; an upper limit exists for the temperature (250°C). Thermal instability is caused by heat sensitive double bonds in the carbon-chain.

It has long been believed that the reaction temperature, or rather the solubility of glycerol in the triglyceride at the reaction temperature, is the determining factor for the yield of monoglycerides. Sonntag (1982) has reported a high yield of monoglycerides in the glycerolysis reactions under distinct conditions ranging from fine dispersion to superemulsion. For an average particle size of 10 to 0.05 microns and smaller, yields of 61 to 95% for monoglycerides is reported. In all cases examined, the fat and glycerol phases are still heterogeneous, although homogeneity is approached at superemulsion range. An interesting conclusion is that high temperature and solubility may not be the only conditions necessary for a high yield of monoglycerides. A high degree of contact may also be a feasible path to high conversion of fats and glycerol to monoglycerides. Therefore, a high shear liquid-liquid contact device is expected to have a positive effect parallel to the solubility effects which result from an increase in process temperature. Consequently, a faster reaction at a lower temperature is expected. Moreover, some of the undesirable taste and color due to the decomposition of triglycerides at high temperatures may be eliminated.

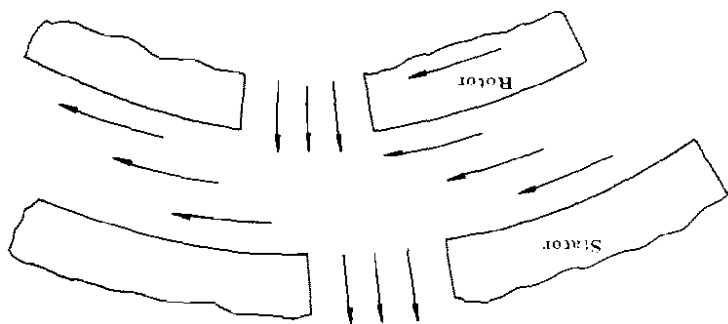
**High Shear Mixing Device** Many industrial processes which utilize triglycerides or their fatty acid derivatives rely on mutual solubility and homogeneity of the liquid phases involved. Consequently, elevated temperature and pressure are used to increase the solubility of the liquid phases involved. Examples where the practical success in the process depends highly on the solubility effects include: (1) triglycerides and alcohol solubility in transesterification and (2) glycerol and triglycerides solubility in glycerolysis. The solubility of the immiscible phases may be achieved by dispersion of immiscible liquids and enhancement of the contact between the phases by mechanical-high shear devices.

A high shear mixing device basically consists of a rotary and a stationary component with a small gap between them. In general both parts are circular in shape with the moving part on the inside. Slots are provided in both parts for flow of the liquid. The gap between the moving and the stationary components, as well as the slots dimensions, will determine the fineness of the dispersed phase. Because of the high speed of the moving component, the liquid to be processed is automatically sucked axially into the dispersing head and is then pressed radially through the gap between the two and eventually exits axially through the slots of the stationary part. Due to the high speed of the rotating part, and the small gap between the two components, the material is subject to very high shearing and crushing forces. The intense turbulence in the gap between the moving and the stationary parts, along with the shearing forces, will lead to an intense mixing of the liquid phases. The decisive factors for the degree of mixing are the speed of



**Biodiesel by-product** By-product recovery has always been a concern in the economics of the biodiesel process. The lower phase from the vegetable oil transesterification process contains about 75% glycerol. Small amounts of esters, alcohol, and impurities from soybean oil are also present. The conventional practice is to recover glycerol by distillation. An alternative for glycerol recovery is to convert the crude glycerol to its mono- and diester derivatives using triglycerides from vegetable oils (glycolysis). The mono- and diglycerides can be made by the reaction of naturally occurring triglycerides, such as soybean oil, with glycerol. Mixtures of mono- and diglycerides with a small percentage of unreacted triglycerides will be formed. The purification step then follows. Therefore, in the by-product recovery flowchart shown below, the first purification step will be eliminated.

Figure 1. Flow Pattern in a Rotor-Stator of a High Shear Device.



the rotating component, the gap between the two components, and the size of the slots on the two components. The average particle size is expected to be under one micron. Figure 1 presents a simple arrangement of a rotor stator assembly.



which are present in the soybean oil and will not interfere with the reactions involved.

There are many commercial applications for the mixed mono- and diglyceride products. Mono- and diglycerides are edible and find use as emulsifiers in foods and in the preparation of baked goods. A mixture of mono-, di-, and triglycerides is manufactured in large quantities for use in superglycerinated shortenings. Mono- and diglycerides are important modifying agents in the manufacturing of alkyd resins, detergents, and other surface-active agents. The monoglycerides are also used in the preparation of cosmetics, pigments, floor wax, synthetic rubbers, coatings, textiles, etc.

## CONCLUSIONS

About 7.8 billion pounds of animal fats are produced annually in U.S. After rendering this yields 5.5 billion pound of tallow and lard. Experimental investigations show that beef tallow can be easily esterified to components with properties similar to esters of vegetable oils (Table 2). A blend of esters of fatty acids and diesel fuel will be helpful to the petroleum industry in meeting the new requirements for lower sulfur, aromatics, and particulates in emissions from diesel engines. This will diversify the current tallow market.

The high cost of biodiesel compared to petroleum diesel has been a major obstacle in the commercialization of biodiesel. Utilization of impure glycerol will make the biodiesel fuel more competitive with the existing diesel fuel market.

The transesterification of triglycerides and glycerol involves two immiscible liquid phases. The degree of contact or solubility of these two phases is the decisive factor for the extent of the reaction. The preliminary investigations show that a high shear mixing reactor will enhance the contact between the liquid phases, which may lead to high yields of monoglycerides. Modifications toward underreaction may also be possible for other reaction conditions such as temperature and reaction time.

Table 2: Physical Properties for Esters of Tallow, Soybean Oils, and Diesel Fuel.

Physical Property	Beef Tallow Esters	Soybean Oil Esters	Diesel Fuel <sup>a</sup>
Density (g/mL) @ 40°C	0.856 - 0.859	0.866 - 0.869	0.835
Viscosity (cP) @ 40°C	3.75 - 3.99	3.70 - 3.90	2.63
Cloud Point (°C)	10 - 12	-1.0 - 1.0	-0.6 - +4.0

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