APPLICATION OF INHERENTLY SAFER DESIGN PRINCIPLES IN BIODIESEL PRODUCTION PROCESS

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Petroleum oil production has increased over the year due to the greater demand. It has been predicted that fossil fuel will be depleted in the near future perhaps as short as 30 years. Increasing demanding, limited supply and associated environmental problems of this fossil fuel are urging us to find alternative energy sources.

Among many of potential energy sources explored, biofuel has been a promising alternative, both economically and environmentally. Biodiesel is typically produced by transesterification that refers to a reaction of a vegetable oil or animal fat with an alcohol in the presence of a catalyst to yield mono-alkyl esters of long chain fatty acids and glycerin. Herein mono-alkyl esters of long chain fatty acids are biodiesel and glycerin is a co-product. The transesterification reaction in biodiesel production can be alkali-catalyzed (i.e., NaOH, KOH) or acid-catalyzed (i.e., H_2SO_4).

The production of biodiesel through the transesterification of vegetable and waste oils have been researched and commercialized. However, most of the studies in the open literature focus on the reaction, production or economic of the process. No papers have addressed the process safety of biodiesel production. Since process safety has been increasingly emphasized in the chemical and petroleum industries, we must consider process safety in the biodiesel industry as well. As Trevor Kletz pointed out (1984, 1991), inherently safer design principles should be considered at earlier stage of process development and process design. This paper reviews the hazards existing in biodiesel production processes and potential inherently safer options and the holistic impact of these options on process safety.

INTRODUCTION

Petroleum derived fuels have been the major energy source in the world since the 19th century. Petroleum production has increased over the years due to the greater demand. It is predicted that fossil oil is to be depleted in the near future as short as 30 years. However, increasing demand, limited supply and associated environmental problems of this fossil fuel are urging us to find alternative energy sources.

Among many potential alternative energy sources, biofuel shows to be a promising one, both economically and environmentally. Biodiesel fuel, as a new biofuel with definite commercial prospects, draws more and more academia, industry, and public interest. According the definition of the American Society for Testing and Materials (ASTM), biodiesel fuel are monoalkyl esters of long chain fatty acids derived from a renewable lipid feedstock such as vegetable oil or animal fat.

Theoretically, vegetable oils and waste oils can be used as a fuel directly. However, they bring a variety of problems, including deposition of noncombustible substances, heavy smoke emission due to inefficient mixing, and injector coking (Barnwal and Sharma, 2005). In particular, the sticky nature (high viscosity) of the straight vegetable oils requires additional precautions and reduces the thermal efficiency of the engine significantly. Research work has been focused on chemically changing the vegetable oils to biodiesel, which has the similar properties to conventional petroleum diesel.
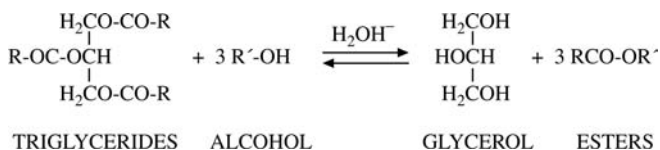
Biodiesel has many benefits due to its unique properties. It is biodegradable, non-toxic, higher octane number with a better combustion emission profile compared to petroleum-based diesel. In particular, less carbon monoxide, sulfur free, no particulate matter and unburned hydrocarbons, which has known to cause environmental degradation, are emitted. Carbon dioxide from combustion of biodiesel can be recycled by photosynthesis (Korbitz, 1999; Agarwal and Das, 2001). The 150°C flash point makes biodiesel less volatile than most petroleum-based diesel, which enhances the safety aspect of transport and handling (Krawczyk, 1996). With the lubricating properties, it can reduce the wear of engine and extend the lifetime of engine. Moreover, its viscosity is close to that of petroleum-based diesel, which makes the direct use of biodiesel in a standard diesel engine possible. It can be used in any concentration with petroleum-based diesel fuel in existing diesel engines after little or no modification (Barnwal and Sharma, 2005). Many researches on improvement of the physical properties of biodiesel fuel are in the open literatures (Korus et al, 1992; Wagner and Shrouch, 1984).

Biodiesel is typically produced by a transesterification reaction of a vegetable oil or animal fat with an alcohol in the presence of a catalyst to yield mono-alkyl esters of long chain fatty acids and glycerin. Herein mono-alkyl esters of long chain fatty acids are biodiesel and glycerin is a co-product. Generally the transesterification of biodiesel production can be alkali-catalyzed (Karmee et al, 2004) or acid-catalyzed (Goff et al, 2004). The production of biodiesel through the transesterification of vegetable and waste oils have been researched and commercialized. However, most of the studies in the open literature focus on the reaction, production or profit of the process. No papers have addressed the process safety of biodiesel production. Since process safety has been increasingly emphasized in the chemical and petroleum industries, we must consider process safety in the biodiesel industry. As Trevor Kletz pointed out (1984; 1991), it is the best to apply inherently safer design principles at an earlier stage of process development and process design.

BACKGROUNDS
There are many processes that can be used for biodiesel production, such as pyrolysis, microemulsification, etc (Oliveira, 2005). Among them, transesterification (or alcoholysis) is the most common way. By this method, vegetable oils or animal fats reacts with alcohol in the present of alkaline, acid, or enzyme catalysts to yield fatty acid alkyl esters called biodiesel and glycerol as a byproduct. The main component of vegetable oils and animal fats are triglycerides, which are essentially a glycerol backbone esterified with three long

chain fatty acids. The corresponding reaction expression is provided herein:

$$H_2CO\text{-}CO\text{-}R \qquad \qquad H_2COH$$
$$R\text{-}OC\text{-}OCH \quad + 3\,R'\text{-}OH \;\xrightleftharpoons[]{H_2OH^-}\; HOCH \quad + 3\,RCO\text{-}OR'$$
$$H_2CO\text{-}CO\text{-}R \qquad \qquad H_2COH$$

TRIGLYCERIDES   ALCOHOL   GLYCEROL   ESTERS

Transesterification of triglycerides from vegetable oils and fats

The oil or fat used in transesterification of biodiesel production can be from any veg-etable oil-bearing material (such as rapeseed, soybeans, cottonseed, peanuts, corn, olives, sesame seeds etc), other oliferous materials, and yellow grease or waste vegetable oils and fats from animal (Ramos and Wihelm, 2005). The alcohol in transesterification must to be monoalkyl, including methanol, ethanol, propanol, butanol, and so on. Transesterification of triglycerides can be catalyzed by a large variety of chemicals including mineral acids, alkaline, alcoxides, Lewis bases, zeolites, metal complexes, strong ion-exchanger resins, functionalized clays, intercalated lamellar double hydroxides, and enzymes (Ramos and Wilhelm, 2005, Suppes et al, 2004). Currently, alkali-catalyzed biodiesel production is the most popular. Many publications discuss the performance of different types of oil or alcohol in transesterification of biodiesel production under various catalysis conditions (Freedman, 1986; Canakci, 1999; Zhang et al, 2003; Goff et al, 2004; Sendzikiene et al, 2004; Karmee et al, 2004).

Kletz (1998) formalized the inherently safer design principles as strategies to remove or reduce hazards at the source instead of add-on controls to achieve inherently safer design. The inherently safer design principles are:

- Intensification/Minimization
  Intensification aims at reducing the quantity of hazardous materials contained in a process or plant. It can be achieved through innovative new technology or improved process design. Usually, intensification is the first thing to consider in inherently safer design since it not only eliminates or reduces the hazards but also economically preferable.
- Substitution
  By substitution, less hazardous or non-hazardous materials are explored to replace hazardous materials. Substitution principles can be applied to process materials, heat transfer fluids, materials of construction, insulation, etc. Sometimes, there is a trade-off between two chemicals when substitution principle is used.
- Attenuation/Moderation
  If intensification and substitution are not possible, attenuation will be the third way. Moderation/Attenuation means storing, transporting, and using hazardous materials under less hazardous conditions or a less hazardous form. Moderation includes dilution, refrigeration, less severe process conditions, etc.

- Limitation
  If an accident does happen, limiting the damage to the minimum level is considered by equipment design or changing reaction conditions.

As a new upcoming industry section, it is imperative to think over how to integrate inherently safer design principles into biodiesel process development and design. In the following sections, existing hazards in some of the current biodiesel processes are discussed, and potential inherently safer options are evaluated qualitatively. Further research is needed to justify each of these options.

EXISTING HAZARDS IN THE CURRENT BIODIESEL PRODUCTION PROCESSES

Four competitively commercial scale processes of biodiesel production are reviewed by Zhang et al (2003), which are developed by using virgin vegetable oil or waste cooking oil and methanol as raw materials under H_2SO_4 or NaOH conditions. The benefits and limitations of each process are discussed by Zhang et al (2003). However, the process designs are compared only from technological and economic aspects. Safety factors are not involved.

To conduct the process safety analysis, the major hazards in the biodiesel industry ought to be identified. The most hazardous materials in the process are methanol, H_2SO_4 or NaOH, which are detailed in the following paragraphs.

Methanol is the most commonly used alcohol to perform transesterification of biodiesel production due to economics. According the MSDS of methanol, it appears as a clear, colorless liquid with flash point of $11°C$ and boiling point of $65°C$. The major hazards of methanol are flammability and toxicity. It can be absorbed by with skin contact or be inhaled through the respiratory system. The contact of methanol may cause defatting of the skin and dermatitis. The inhalation of methanol can cause adverse central nervous system effects, including headache, convulsions and possible death, cause visual impairment and possible permanent blindness. It can also cause irritation of the mucous membrane.

H_2SO_4 or NaOH are normally chosen as catalysts in the process of biodiesel production because of their effectiveness and economics. Both chemicals are toxic, but not volatile. Concentrated H_2SO_4 and NaOH solid can cause severe burns upon contact with skin. Corrosion of H_2SO_4 or NaOH in the present of water is also an important hazard in the process. Acid residues present in the biodiesel can damage diesel engine parts (Al Saadi and Jeffreys, 1981).

INHERENTLY SAFER OPTIONS

Integration of inherently safer design is always preferred over add-on engineering controls. In this section, biodiesel production processes are reviewed against inherently safer design principles. Further research, experiment and pilot testing are needed to justify these options.

INTENSIFICATION

The transesterification of vegetable oils to biodiesel is a relatively slow reaction. The reactant (alcohol) needs to be excessive in order to drive the reversible reaction in the preferable direction. The residence time of the reactor can be as long as several hours (Zhang et al, 2003). In the transesterification reaction, the reactants initially form a two-phase liquid system. As the reaction continues, the esters formed may serve as a mutual solvent for the reactants and a single-phase system develops. As concluded by Noureddini and Zhu (1997), the transesterification of soybean oil is an initially mass transfer-controlled region followed by a kinetically controlled region. Enhanced mixing will be beneficial to achieve smaller reactor size and shorter residence time, especially in the initial stage of reaction. Moreover, improved mixing performance will require less alcohol to achieve the ultimate conversion, thus reduce the hazards from excess alcohol.

The application of process intensification on biodiesel production can be realized by using a continuous oscillatory flow reactor (OFR), which was proposed to improve mixing, and therefore heat and mass transfer factors (Harvey et al, 2003). OFR consists of tubes of equal spaced orifice plate baffles. It applies oscillatory motion upon the net flow in a plug flow reactor to increase heat and mass transfer by creating flow patterns. OFR design can eliminate the dependence of the degree of mixing on the net flow, compared to the conventional plug flow reactor that must maintain a minimum Reynolds number to obtain good mixing of oil and alcohol. The application of OFR will reduce the diameter-to-length dimension of the reactor. For many current biodiesel production performed in batch process, OFR can convert them to a continuous process by intensifying process by improving mixing. In the Harvey et al study, the transesterification of rapeseed oil and methanol with NaOH as catalyst is examined. They found that OFR was suitable for biodiesel production of vegetable oil and possesses lower residence time than batch processes at the designed conversion level.

Methanol imposes both toxicity and flammability hazards. In particular, excessive methanol is required to achieve a reasonable conversion. Alkaline catalysts require less methanol and the alkali-catalyzed transesterification is much faster than the acid catalyzed reaction (Oliveira et al, 2005). In this regard, alkaline catalysis is preferred. However, free fatty acids in the raw materials, especially waste oils, will react with alkaline catalysts and form soaps. This soap inhibits the reaction and the separation of the products. Therefore, alkaline catalysis is not the optimal option if waste oil is not pretreated (Canakci and Gerpen, 1999; Zhang et al, 2003).

Supercritical transesterification does not need the presence of catalyst, thus eliminate the hazards associated with acid or alkaline catalyst (Barnwal and Sharma, 2005). The amount of methanol required to achieve a certain conversion may be much larger than a conventional catalyzed transesterification. A normal continuous alkali-catalyzed process needs the feedstock of 6:1 molar ratio of methanol to vegetable oil for 98% conversion (Zhang et al, 2003). However, with applying the supercritical methanol method, the 95% conversion takes place with a molar ratio of methanol of 42 for the case of rapeseed oil at a critical temperature of $350°C$ (Barnwal and Sharma, 2005). Moreover, the

temperature and pressure are elevated to achieve the supercritical state (for the supercritical methanol, at temperature of 239°C and pressure of 8.09 MPa), which may increase the potential flammable hazard to the system due to the low flash point of methanol.

SUBSTITUTION

Although methanol is commonly used to react with triglycerides to produce methyl ester, other alcohols can be used to esterize triglycerides to obtain biodiesel. To replace methanol with other alcohols may reduce the toxicity and flammability hazards. Ethanol, 2-propanol, and n-butanol tranesterification have been reported to be promising (Tashtoush et al, 2004; Canakci and Gerpen, 1999; Freedman, Butterfield, and Pryde, 1986). Gauglitz and Lehman (1963) found that the rate of transesterification with longer chain alcohols have longer reaction times at the same temperature. They showed that the addition of one methylene group to the alcohol doubles the reaction time and the addition of a branched chain quadruples the reaction time. However, it is also reported that etherification reaction will be slower with ethanol or other alcohols compared with methanol at the same condition (temperature). However, with the increasing molecular weight, the boiling point of the alcohol is higher, which enables higher operating temperature. The increase in the reaction rate and conversion due to temperature rise actually overrides the slowing down due to the substitution (Canakci and Gerpen, 1999). To further justify the substitution, more experiments, comprehensive research, economical consideration are required.

It is known that this transesterification reaction is catalyzed by many chemicals. Currently mineral acid (mainly sulfuric acid) is usually transported and stored in the concentrated form to reduce associated cost and corrosion. However, mineral acid can cause serious personal injury and pose a health and safety hazard. In particular, residue acid in the biodiesel may corrode the engine and shorten lifetime of the engine. Different catalysts have been explored (Suppes et al, 2004; Goff et al, 2004; Sendzikiene et al, 2004). Their data shows that the reaction rate depends on the concentration of the catalyst and the acidity of the reaction mixture (Sendzikiene et al. 2004). Less hazardous organic acids may not be effective catalysts. However, more comprehensive study is needed to find an ideal substitute.

ATTENUATION

In general, transesterification reaction is faster and the conversion is higher at higher temperatures and pressures (Noureddini and Zhu, 1997; Suppes et al, 2004). Between alkaline and acid catalyzed processes, acid normally requires higher temperature and pressure to achieve the same conversion. Experimental data shows that overall conversion increases with temperature, and reaches an asymptotic value at about the boiling temperature of the alcohol. However, operation conditions which is near the boiling point of methanol poses public hazards upon leaking. Inherently safer design suggests lower equipment cost and lower energy cost. Slower reaction time may actually be a benefit because a single operator

may be able to sequentially handle several parallel batch reactors during his operational shift. Process simulations are required to find the economic optimal point with the safety constraints.

LIMITATION

Limitation of harmful impacts is primarily determined by production size rather than specific parameters of the transesterification process. While proper mitigation measures need to be in place, the facility and process must be designed to minimize the effects of the released hazardous materials and energy. Plant layout and equipment design must be scrutinized to minimize the size, probability, and effects of any toxic or flammable material releases. There are some general guidelines, but essentially limitation measures depend on particular facility and process.

CONCLUSIONS

Proposed processes are reviewed against inherently safer design options. However, many options have tradeoff between the safety, operability, and economics. The inherently safer options can only be decided with feedstock characteristics, further experiment, research, and pilot testing.

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