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Consequence modeling of hazardous accidents in a supercritical biodiesel plant

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HIGHLIGHTS

- Jet fire was identified as the most likely incident in the case of flammable material release.
- It was recommended to minimize the number of workers and the work hours in vicinity the possible source of release.
- For equipment and structure protection, it was recommended to minimize the flammable material inventory.
- Provide proper isolation systems and using fireproofing coatings.

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ABSTRACT

Biodiesel is going to be one of the most preferable fuels because of fossil fuel sources depletion and rising environmental issues. This type of fuel is produced mainly by transesterification of triacylglycerol compounds such as vegetable oils and animal fats in a catalyzed or non-catalyzed reaction media. Energy, cost and environmental investigations for conventional (catalyzed) and modern (non-catalyzed) methods show that non-catalyzed method in supercritical process conditions is more advantageous but more unsafe because of high pressure and high inventories of flammable materials. Thus, this paper is aimed at identifying and analyzing the severity of process incidents in a supercritical biodiesel plant using consequence modeling and analysis approach. Following this approach, pressurized liquid inventories were identified as the most hazardous sources and subsequently jet fire was identified as the most likely incident in the case of flammable material release. Then, destructive effects of jet fire were simulated for three different leakage sizes from 0.5 to 1.5 inch. The results showed long effect distances, the ranges of which were 61–159 m and 70–190 m for the structures and humane respectively. According to these results, in the case of jet fire, structures and humane in a long distance around the source of release would be affected. Thus, all human in these areas shall leave the mentioned distances in less than few seconds which seems to be impossible. Also, structures and equipments would be damaged if flame impingement duration lasts more than 2 s. Therefore, sufficient protections should be provided to decrease the level of Jet Fire damage on near structures and personnel. Besides, supercritical biodiesel plants should be designed in a low production capacity in order to decrease the hazardous radios and the duration of feeding the release source in the case of any risk.

1. Introduction

Nowadays, rapid growing of energy consumption has been a critical concern since the limitation of known fossil fuel sources alerted major consumers. Regarding that fossil fuel sources have the greatest share in energy consumption, decreasing of such sources makes the renewable energy alternatives more attractive [1]. In addition, concerns about environmental issues increase the interest for replacing of such energy sources mostly because of greenhouse gases emission [2]. Although there are plenty of renewable energy sources which are being used efficiently by industries, biodiesel is among the most desirable alternative energy candidates which can be extensively used in diesel engines as a transportation fuel in future [3].

Biodiesel is produced by transesterification of triglycerides [2] from different vegetable oils and animal fats. Oil of edible

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vegetable seeds like soybean, sunflower, rapeseed or, non-edible seeds like jatropha, cottonseed, and castor could be used as feedstock. The transesterification reaction can be non-catalyzed or catalyzed by a base, an acid or an enzyme [4,5]. The catalyzed reactions which are conventional method of transesterification can be done as one-step or two-step (esterification by acid then transesterification with base) processes, dependent on the content of FFA. The two-step process is recommended if a feedstock contains more than 1% of FFA [6] in order to avoid saponification event. It should be mentioned that there is an alternative method of transesterification that is performed under supercritical conditions [7].

As a significant advantage, supercritical method could be used for the conversion of low price feedstocks which have large amount of free fatty acids as well as other oils. The price of feedstock has a major influence on the final biodiesel price that is about 60–80% of the total cost [8]. Oil should be extracted from oily seeds to convert into biodiesel in the conventional method, but supercritical method could be integrated with oil extraction. In the other words, in situ transesterification is possible in supercritical method. Moreover, Supercritical conversion, also, has environmental advantage as no toxic solvent is needed for the oil extraction unlike the conventional method [9]. Integration of the transesterification with oil extraction or using low price oils with high content of FFA as feedstock makes the supercritical method to seem more economic expensive in comparison with conventional transesterification. Energy consumption and thus the cost of biodiesel production in supercritical and conventional method should be investigated for comparison as there are some trade-offs. In supercritical condition, temperature and pressure are very high (for example 250 °C and 10 MPa), on the other hand the reaction is very rapid; conversely, in the conventional transesterification, the conditions are atmospheric and moderate temperature (about 60 °C) but it takes the reaction a long time to be completed. Energy consumption of the two technologies was evaluated and seemed to be followed by almost the same content [10].

Mentioned factors compare two methods from the point of energy, cost and environment and it seems that supercritical method has many advantages but there is another important factor of safety that its ignorance might cause serious problems such as fatalities, injuries and loss of products [11]. So, there is a critical need to conduct safety studies for biodiesel production factories to prevent or mitigate such effects. Recently, researchers have been motivated to carry out some safety evaluation studies for the conventional transesterification which is the biodiesel production method in the industry. This motivation is mostly because of the growing number of this type of biodiesel production factories and some reported destructive incidents of fire and explosion [11,12]. In such processes, relatively high temperature, high inventory of flammable materials and high corrosion in acid process seem to be hazard sources. Historical analyses of biodiesel factories, with respect to the plant operations, demonstrate that approximately all accidents refer to methanol vapors. In some cases, domino effects generated fires of oil stored in the plant [11]. From 2006 to 2009, about 21 accidents occurred in the form of fires or explosions [12] that nearly half were linked to improper handling or containment of hazardous chemicals [12]. More specifically, in the year 2009 two accidents were reported in USA. First, in the 17th of the July, in the Columbus Foods Plant of Chicago, two workers were injured while mixing chemicals. Second, in the 24th of the September, fire and explosion happened in the warehouse containing tons of methanol and biodiesel in the New Eden Energy plant of St. Cloud [11]. Moreover, in 3-year period (2006–2009) there were 8 fires and 6 explosions in biodiesel facilities in the U.S., i.e. 5 incidents per year [11].

Although there have been some safety studies for conventional biodiesel production facilities, there are still unmet safety studies for supercritical transesterification type of biodiesel plants. Considering that supercritical biodiesel plants are in the step of scale up and design, such safety studies seem very valuable at this early stage. In such processes, very high pressure and temperature and high inventory of flammable materials are taken into account as the hazard sources. High pressure controlling is a great challenge in the chemical processes which may cause undesirable consequences. So, it is clear that supercritical process is more unsafe in comparison with the conventional transesterification. Therefore, this paper is aimed at identifying the types and then estimating the severity of likely process incidents in a supercritical transesterification biodiesel plant. And then, safe distances around such plants can be identified and necessary precautions can be recommended to decrease the level of hazard. For this purpose, a well known procedure of consequence modeling and analysis [13] is used by PHAST software Ver 6.54.

2. Supercritical transesterification biodiesel production

2.1. Transesterification reaction

Transesterification is a chemical reaction (Fig. 1) which converts Oil (Triglyceride; represented by Triolein in simulation) and Alcohol (Methanol) to Biodiesel (Fatty Acid Methyl Ester, FAME; represented by Methyl Oleate in simulation) and Glycerol. Typically, Alcohol is used in excess to shift the reaction forward to attain a high yield of Biodiesel. Basic catalyzed reactions are more rapid and less corrosive but could not be used for the Oils with a great amount of free fatty acid. In catalyst free reaction, which is the scope of this study, Alcohol should be in supercritical conditions. The schematic of the reaction is show in Fig. 1.

2.2. Process flow sheet of supercritical methanol process

To obtain the relevant data for the safety analysis of the supercritical process, the process flow sheet which is developed by Kiwjaroun et al. is adopted [14]. The process, as outlined in Fig. 2, is mainly composed of one reactor and two distillation columns. Oil (12,500 kg/h) and Methanol (1490 kg/h) are compressed up to 19,300 kPa and preheated. Fresh Methanol is mixed with recycled Methanol to make the 1:42 ratio of Oil to Methanol before feeding to the reactor. The reaction takes place at 300 °C. The products are sent to heat exchangers to transfer excess heat to the feeds, and then are fed to a distillation column. Methanol is separated from the top of the column and sent to a heat exchanger to preheat before recycling to the reactor. The bottom products of this column, Biodiesel (90%) and Glycerol (10%) are sent to the second distillation column to separate Biodiesel (99.5% pure, 12,520 kg/h) from Glycerol (93% pure, 1473 kg/h). The stream properties and composition are shown in Table 1.

3. Consequence modeling and analysis

Consequence modeling and analysis refers to the numerical estimation of physical outcomes due to any loss of containment involving flammable, explosive and toxic materials with respect to their potential impact. Some conditions may lead to undesirable releases which, under specific circumstances, can progress to serious incidents. Such incidents might threaten employee safety, nearby residents, property and the environment. In order to evaluate the consequences of such likely incidents, some sub-studies should be carried out as shown in Fig. 3. Subsequent detailed required data for carrying out such studies for a supercritical biodiesel production facility are described in following sections.