Consolidation of available methods and design of a reliable physicochemical system for transesterification progress monitoring in biodiesel reaction chamber

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Abstract - Biofuel extracted from non-edible vegetable oils and animal fats is an attractive alternative fuel. Sustainability of biodiesel extraction is very much required today. The present biodiesel extraction plants need government subsidies to make them profitable by the producers and to be affordable by the public. The root cause of non sustainability is energy intensive process steps involved in the production of biodiesel. Most of the plants in India use batch process method of transesterification. Monitoring transesterification process states and stages is very much required to reduce the time and energy consumption. Researchers have suggested some of the technical methods as monitoring of refractive index, specific gravity, viscosity, pH, and electric impedance. This paper discusses all these available methods and their advantages and disadvantages. It also discusses the consolidation of these methods and presents a reliable physicochemical system for the purpose of online monitoring of transesterification process progression. Advantages of such system are also discussed.

Key Words: Biodiesel, batch process, transesterification progress, viscosity, impedance, pH

1. INTRODUCTION

Prices of petroleum products are unstable and ever increasing. On the other side, due to the increasing world population, quest for the better living standard and several other reasons, the demand for petroleum is on the increase daily. Petroleum and allied fuels are also posing threats to environment. World is facing the dangerous energy crisis sooner. This has given way to the search for alternative sources of new, sustainable and renewable energy such as biomass, solar, hydro, wind and tidal sources. In recent years biodiesel production from non-edible vegetable oils and animal fats has gained significant momentum throughout the world.Monoesters produced by the transesterification of vegetable oil with alcohol are known as biodiesel fuels [1]. The general method to produce biodiesel is transesterification of non-edible oil with methanol in the presence of either base or strong acid catalysts. Transesterification reaction is quite sensitive to various parameters. An ideal transesterification reaction differs on the basis of variables such as fatty acid composition and the free fatty acid content of the oil. Other variables include reaction temperature, ratio of alcohol to vegetable oil, catalyst, mixing intensity, purity of reactants. Biodiesel is a biodegradable and renewable fuel. It contributes no net Carbon Dioxide or Sulfur to the atmosphere and emits less gaseous pollutants than normal diesel. Carbon dioxide, aromatics, polycyclic aromatic hydrocarbons (PAHS) and partially burned or unburned hydrocarbons emissions are all reduced in vehicles operating on biodiesel [2]. Varieties of feed stocks such as vegetable, animal fats and non edible oils are tried and some are feasible and commercially viable [3]. Biodiesel production from Neem (Azadirachta Indica) seed oil is an attractive one as the Neem trees are largely grown in India. Contribution of Neem seed oil as a source for biodiesel production has gained lots of importance in India. Shruthi et al. have discussed the prospects of Neem seed, method of biodiesel production from crude Neem oil. The fuel properties of biodiesel from Neem oil including flash point and fire point are studied and presented. The engine properties and emission characteristics under different biodiesel percentages were also studied and presented [4]. Honge (Pongamia Pinnata/ Millettia Pinnata) seed, also known as Karanja seed, is a promising feed stock for transesterification of biodiesel. Honge is a normal sized tree basically used to stop soil erosion by planting them along the highways, roads and canals. The honge seeds contain about 30-32% oil. It is well-adapted to arid zones and has many traditional uses. It is often used for landscaping purposes as a windbreak or for shade due to the large canopy and showy fragrant flowers. These trees can also be grown on waste, barren lands and arid plains. Honge trees are largely grown in North Karnataka in India. The plantation scope and sustainability are narrated by Vigya Kesari et al. [5]. Various types of seed oils and fats are tried and tested Out of them, Pongamia Pinnata can be a definite source of raw material due to its easy availability in wild. Detail study made by Bobade S. N. et al. intends to identify all advantages and disadvantages of Pongamia Pinnata as a sustainable feedstock for the production of Biodiesel equivalent to fossil fuel as per ASTM 6751-9B [6]. The various aspects of Pongamia as potential fuel in India are discussed by Gaurav Dwivedi et al. The study has revealed that brake specific fuel
consumption and brake thermal efficiency of B10 biodiesel from Pongamia is comparable to diesel. The hydrocarbon and carbon monoxide gas emissions are quite low in case of Pongamia biodiesel as compared to diesel [7]. After transesterification of crude oil from Pongamia seeds show excellent properties like calorific value, iodine number, cetane number and acid value etc. Detail study intended to identify all advantages and disadvantages of Pongamia Pinnata as a sustainable feedstock for the production of Biodiesel equivalent to fossil fuel as per ASTM 6751-9B is presented by Bobade S.N. et al. [8]. Various other non-edible seed oils are also tried and researches are able to present a method of biodiesel extraction. Biodiesel production and fuel properties from non-edible Champaka (Michelia Champaca) seed oil for use in diesel engine is explained by Siddalingappa et al. [9].

2. NEED FOR ONLINE TRANSESTERIFICATION PROCESS

Sustainable biodiesel extraction is the need of hour today. Current biodiesel technologies are not sustainable as they require government subsidies to be profitable by the producers and to be affordable by the public. In order to reduce production costs and make it competitive with petroleum diesel, low cost feedstock, non-edible oils and waste cooking oils can be used as raw materials. Net energy benefit can be increased by using high oil yielding renewable feedstock like algae. Main reason for non sustainability is energy intensive process steps involved in the production. Veera Gnaneswar Gude et al. have also suggested the process optimization using novel heating and mixing techniques, and net energy scenarios for different feedstock from sustainability view of the biodiesel production technologies [10]. A sustainable biodiesel production must:

- Utilize energy-efficient, non-conventional process stages
- Use online calculation of FFA in raw seed oil
- Adopt continuous online monitoring of extraction stages and
- Provide faster and efficient esterification process.

Most of the biodiesel plants in India are either offline or semi-automated. They require both human monitoring and intelligence in several aspects and stages. There is an immediate need and scope for

- Mini extraction plant which can be financially and technically feasible for any individual or local authority/agency
- Speeding up the transesterification process
- Maintenance of quality of esterification process.

3. AVAILABLE METHODS OF MONITORING TRANSESTERIFICATION PROGRESS/STATUS

The monitoring of the reaction status of biodiesel transesterification progress will minimize the time and increase the energy efficiency of conversion. Researches around the world have consistently working on several physicochemical methods of monitoring the reaction stages and status. The following section discusses such available methods and their advantages and disadvantages. The monitoring of the reaction status of biodiesel transesterification progress will minimize the time and increase the energy efficiency of conversion. Researches around the world have consistently working on several physicochemical methods of monitoring the reaction stages and status. The following section discusses such available methods and their advantages and disadvantages. The review paper by Alemayehu Gashaw et al. describes the fuel properties of biodiesel, production process (transesterification) and the most important variables that influence the transesterification reaction. Transesterification reaction is quite sensitive to various parameters. An ideal transesterification reaction differs on the basis of variables such as fatty acid composition and the free fatty acid content of the oil. Other variables include reaction temperature, alcohol to vegetable oil ratio, catalyst, mixing intensity, and purity of reactants [11]. Continuous low cost transesterification process for the production of coconut biodiesel is studied and implemented by Gajendra Kumar et al. This research work was aimed to characterize a system for continuous transesterification of vegetable oil from coconut using five continuous stirring tank reactors (CSTRs). This work shows that a high stirring speed increases the reaction rate, but an excessive stir speed decreases the reaction rate and conversion to biodiesel. It also points out that a higher catalyst percentage significantly increases the reaction rate and production capacity. The biodiesel produce from coconut oil was characterized for their physical and fuel properties including density, viscosity, iodine volume, acid volume, cloud point, pour point, gross heat of combustion, and volatility. Further, the purity and conversion of the biodiesel was analyzed by HPLC [12]. This paper gives a glimpse of idea that reaction rate can be controlled and physical properties can be used for reaction monitoring. HPLC method of analysis cannot be adopted for small continuous esterification plant due to the cost and total investments. Rouhollah Ghanei has described the changes of physical properties during transesterification reaction and validated his results with transesterification of sunflower, canola and corn oils was carried out at 65°C, MeOH to oil molar ratio of 6:1, 1 wt% of KOH as catalyst under vigorous mixing for 60 minutes. The paper suggests that the progress of transesterification of oil to biodiesel could be determined by monitoring the physicochemical changes during reaction as an alternative to expensive and time-consuming methods. Specific gravity, viscosity, refractive index, cloud point, pour point and flash point of six blends were measured and the appropriate functions were fitted on the extracted data. Results have shown that the physical properties of fresh oil change during the reaction with a constant rate and the slope of the changes are independent of oil type. Depending
The completion of transesterification process and the conversion to biodiesel are immersed in the feedstock and an AC excitation voltage is applied across the interleaved electrodes producing an oscillating electric field. The voltage developed across a series resistor is measured and correlated to two important phases of the transesterification reaction, a mass transfer control phase followed by a kinetically controlled phase. The sensor proposed by them is very simple to fabricate, has no moving parts and requires relatively simple electronics. The resulting measurement data is very useful for the control of early stages of the transesterification process and the detection of steady state conditions.

4. CONSOLIDATION OF EXISTING METHOD

VAILABLE METHODS OF MONITORING TRANSESTERIFICATION PROGRESS/STATUS

Density and viscosity changes, infrared and laser absorption/reflection/transmittance are tried and proved to be means of monitoring the biodiesel transesterification progress by many researchers around the world. But, these methods are not suitable for small continuous biodiesel extraction plants in India either due to the non specificity or high investment cost. Methods such as monitoring of changes in viscosity, impedance and pH change are commercially viable and technically acceptable. But these methods are tested for the compliances at laboratory on bench or in vitro level. The detailed study reveals that the use of such sensors to detect the process steady state in an actual transesterification plant will result into saving energy during the process by monitoring of reaction stages and or end point. This will lead to energy efficiency, and the quality of biodiesel produced. Using these methods together and correlating the result to the reaction progress to an acceptable level, is quite useful such plants. Hence, we are proposing a consolidation of these three methods and averaging their indication as a viable means.

In our previous technical paper, we have identified various points of considerations for automating the batch transesterification plant. The paper has also discussed complete automation from the starting point of handling the raw oil to the production of biodiesel. The schematic representation of an automation system was proposed. It was also concluded that the foremost important aspect of automation is the effective monitoring of transesterification stages [20].

Figure 1 shows schematic arrangement of a reliable physicochemical system for transesterification progress monitoring in biodiesel reaction chamber. It uses systematic consolidation of monitoring of three parameters in order to indicate the reaction progress. This will greatly optimize the esterification process both in terms of time and energy. A viscosity probe, a comb shaped indigenously developed impedance electrode and a pH probe will be used for implementation. The analog signals are processed and converted to digital data to interface them to a central processor. The processor is a microcontroller unit which sequentially selects one sensor output on a time slot base via a multiplexer.

Measurement of pH value of feedstock during the reaction is an attractive and simple method to monitor the reaction. This is experimentally done by William M. Clark. Transesterification of canola oil at 6:1 methanol to oil ratio with 0.5 wt. % KOH as catalyst was studied at 25°C, 35°C, and 45°C. Reaction conversion was correlated to pH measurements and the results were shown to be in agreement with an independent measure of conversion using an enzymatic assay for glycerol. Rate constants obtained from these measurements are consistent with those in the literature. The measured pH change appears to be related to dilution of OH ions as the oil is converted to products rather than to depletion of OH due to reaction [18].

Information regarding the progress of mass transfer and chemical reaction during biodiesel production can be obtained by measuring the impedance of reactant in the chamber using a simple impedance sensor. This method is proposed and tested by Rachmanto et al. It uses a simple impedance sensor consisting of two sets of interleaved electrodes (comb shaped) separated by a gap. The electrodes are immersed in the feedstock and an AC excitation voltage
The progress of transesterification and the end point will be indicated on an LCD display. The operator will be able to turn off the agitator, a temperature controller. None of the individual measurement is scientifically perfect as the indication depends on several other physical and chemical conditions. Hence the proposed system will ensure that the estimation of reaction progress and end point is acceptable for all practical purposes. It is because that this system cross checks the estimation by three methods. This can also be made as auto shut off so that greater precision is achieved.

5. CONCLUSION

The proposed system is a systematic consolidation of three different ways of transesterification progress monitoring. It is reliable for all practical purposes and is a big step towards online conversion of batch process type esterification. It reduces both time and energy involved in biodiesel extraction and hence, highly suitable for extraction plants in India.

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REFERENCES


