PROPOSTA EMPÍRICO/TEÓRICA PARA A PRODUÇÃO DE BIODIESEL

EMPIRICAL / THEORETICAL PROPOSAL FOR THE PRODUCTION OF BIODIESEL

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RESUMO

O presente manuscrito representa a projeção de experimentos de laboratório em um reator teórico projetado para a produção de biodiesel. Os objetivos deste projeto foram: produção de biodiesel em menos tempo; menor consumo energético para a produção de biodiesel; não dependência da cinética reacional da temperatura de reação e taxas de conversão elevadas de matéria-prima em produto final com reações de transesterificação realizadas nos limites estequiométricos. Os resultados apontam que a utilização de um único vaso reacional para a realização de diversas etapas da produção sem a transferência da massa total de fluido combustível entre diversos vasos reduz o tempo total de produção. O tempo também foi otimizado com a utilização de um sistema de monitoramento adequado. Realizar as reações próximo aos limites estequiométricos reduziu o tempo de refino do produto final, pois existe menos matéria-prima para ser removida do produto final. O monitoramento da reação com espectroscopia LASER em tempo-real permitiu iniciar a reação a temperatura ambiente e aumentar o fornecimento de energia (calor) ao longo da reação, diminuindo o consumo de energia durante a reação, e, o ponto de equilíbrio foi detectado com facilidade pelo sistema de monitoramento.

Palavras-chave: *Produção de biocombustíveis, espectroscopia LASER em tempo real, design de reator, economia de energia, otimização de tempo*

ABSTRACT

The present manuscript represents the projection of laboratory experiments in a theoretical reactor projected for the production of biodiesel. The objectives of this project were: production of biodiesel in less time; to reduce the energy consumption into the production of biodiesel; Non-dependence of the reaction kinetics from the reaction's temperature and high conversion rates of raw material into the final product with transesterification reactions performed at stoichiometric limits. The results indicate that the use of a single reaction vessel to perform several stages of production without the transfer of the total mass of fuel fluid between several vessels reduces the total production time. The reaction time was also optimized with the use of an appropriate monitoring system. Performing the reactions near the stoichiometric limits reduced the refining time of the final product, as there are fewer raw materials to be removed from the final product. Monitoring of the reaction with real-time LASER spectroscopy allowed initiating the reaction at room temperature and increasing the supply of energy (heat) throughout the reaction, reducing the energy consumption during the reaction, and the moment of chemical balance was detected with the monitoring system.

Keywords: *Biofuel production, real-time LASER spectroscopy, reactor design, energy saving, time optimization*

INTRODUCTION

I am writing this paper to attend a request from a friend, there is a long time that I don't write about biodiesel, therefore at this point in time, this manuscript may just be obsolete.

The present manuscript is a condensate of different experiments related to the production of biodiesel. The aim of this manuscript is to demonstrate alternative theoretical and empirical means to produce biodiesel faster, with lower energy consumption while maintaining the quality of the final product.

Familiarization with a real-time LASER spectroscopy technique will facilitate the understanding of the mechanisms proposed by this paper to execute the follow-up of the transesterification reaction. A suggested reference to get acquainted with it is in "Monitoring the transesterification reaction through multiple sensors data integration" (De Boni, 2012).

A theoretical model for a reactor utilization described in the Brazilian patent PI 1005559-2 A2 (2010) is proposed, aiming the production of the biofuel with the conversion rate of triglycerides to monoalkyl esters higher than 99%. Figure 1 shows the reactor and its components, off-scale.

Some minor modifications have been added to the original design to facilitate identification of phase separation of the products (biodiesel/glycerin), through the use of a larger number of sensors like in Brazilian patent PI 1004415-9 A2 (2010).

The material proposed for the construction of such theoretical reactor is described in the Brazilian patent PI 1005075-2 A2 (2010), it is a lightweight composite, possessing characteristics of thermal isolation, low electrical conductivity, and resistance to chemical attacks.

The proposed microcontroller to monitor the reaction and control the reactor is an Arduino Mega, because it is affordable. The software used to monitor the reaction was the Lorscheiter Viewer 1.0, available at <<http://deboni.he.com.br/lviewer/>>. The source code of the Arduino can be ordered from the Jumpear Tecnologia Company, available at <<http://www.jumpear.com.br/>>.

DEVELOPMENT

The present experiment was conducted in the laboratory and the lab results were scaled up to the proposed reactor. Commercial soya bean oil (triglyceride), potassium hydroxide (catalyst) and methanol (alcohol) were used. The chemical reaction that occurred in the reactor was transesterification.

Considering Figure 2, the generalized aspects of the system, the following operations are carried out to produce biodiesel in this reactor:

1. Whereas, the catalyst is prepared in the mixer vessel (6) of Figure 2. Add the volume of methanol contained in the vessel 5 of Figure 2 to the reactor. For this experiment it was used 130ml;
2. By titration, determine the mass of catalyst, stored in the vessel (4) of Figure 2, to be used;
3. Add the catalyst (KOH) to the methanol, in this case it was used approximately 10g;
4. Dissolve the catalyst in methanol for *in situ* production of the catalytic mixture;
5. Add the oil to the reactor;
6. Activate the reactor agitation system;
7. Turn on the reactor heating system. The initial oil temperature was 20,64 °C (69.15 F);
8. Activate the reaction monitoring system(real time LASER spectroscopy);
9. Under constant stirring add the previously prepared catalytic mixture to the reactor. (Date of acquisition of the data 9/27/2011 Time that the first transesterification reaction started: 10:55:57 HH:MM:SS. End of the monitoring time: 12:58:37 HH:MM:SS. Sample points 7082. Total obtained data: 63738 points. Total monitoring time: 2:02:40 HH:MM:SS)
10. Allow the reaction to proceed with increasing temperature until the chemical balance is established by the monitoring

- system (graphic example in Figure 3). Temperature at chemical balance 57.31 °C (135.16 F);
11. After the reaction reaches chemical balance, turn off the stirring system and heating system;
 12. Activate the electrostatic separation system;
 - a) Simultaneously initiate the preparation of the catalytic mixture for the second transesterification reaction.
 - b) Repeat steps 1-4 by adjusting the volume of the reagents to 26 ml of methanol and 2 g of KOH.
 13. Allow the separation of glycerin and biodiesel;
 14. Separation of the glycerin is readily determined by the optical system, a sharp variation in absorbance indicates that the glycerin has been separated (example in Figure 3);
 15. After the glycerin separation from the biodiesel phase, turn off the electrostatic separation system;
 16. Move the glycerin into the vessel 15 of Figure 2;
 17. Maintain the product of the first transesterification reaction in the reactor. Believe that it's purity is not less than 80% conversion of raw material into fuel or make an H¹NMR test to confirm (De Boni *et al*, 2013)
 18. Activate the reactor agitation system;
 19. Start the heating system of the reactor. The initial temperature in the second transesterification reaction was 39.01 °C (102.21 F);
 20. Activate the reaction monitoring system;
 21. Under constant stirring add the previously prepared catalytic mixture to the reactor. (Date of acquisition of the data 27/9/2011 Time that the second transesterification reaction started: 13:09:35 HH:MM:SS. End of the monitoring time: 14:32:38 HH:MM:SS. Sample points 4798. Total obtained data: 43182 points. Total monitoring time: 1:23:03 HH:MM:SS);
 22. Allow the reaction to proceed, with the elevation of temperature, until the chemical balance is established by the monitoring system (graphic example in Figure 5). The temperature at chemical balance was 56.31 °C (133.36 F);
 23. After the reaction reaches the second chemical balance, turn off the stirring and heating system;
 24. Activate the electrostatic separation system
 - a) Simultaneously initiate the preparation of the catalytic mixture for the third transesterification reaction.
 - b) Repeat steps 1-4 by adjusting the volume of the reagents to 5 ml of methanol and 0.4 g of KOH.
 25. Allow the separation of glycerin and biodiesel;
 26. Separation of the glycerin is readily determined by the optical system, a sharp variation in absorbance indicates that the glycerin has been separated (example in Figure 5);
 27. After the glycerin separation from the biodiesel phase, turn off the electrostatic separation system;
 28. Conducting the glycerin into the vessel 15 of Figure 2;
 29. Maintain the product of the second transesterification reaction in the reactor. Believe that it's purity is not less than 96% of conversion of raw material into fuel.
 30. Activate the reactor agitation system;
 31. Activate the reactor heating system. The initial temperature in the third transesterification reaction was 32,02 °C (89.63 F) (Figure 6);

32. Activate the reaction monitoring system
33. Under constant stirring add the previously prepared catalytic mixture to the reactor (Date of acquisition of data 27/9/2011. Time that the third transesterification reaction started: 14:40:05 HH:MM:SS. End of the monitoring time: 16:48:13 HH:MM:SS. Sample points 7397. Total obtained data: 66573. Total monitoring time: 02:08:08 HH:MM:SS);
34. Allow the reaction to continue, with the elevation of temperature, until the chemical balance is established by the monitoring system (there is a graphical example in Figure 6). The temperature at chemical balance was 56,05 °C (132.8 F);
35. After the reaction reaches the second chemical balance, turn off the stirring and heating system;
36. Activate the electrostatic separation system;
37. After the glycerin separation from the biodiesel phase, turn off the electrostatic separation system;
38. Conducting the glycerin into the vessel 15 of Figure 2;
39. Maintain the product of the third transesterification reaction in the reactor. Believe that its purity is not less than 99% conversion of raw material into fuel.
40. Switch on the stirring system
41. Turn on the low-pressure system;
42. Use the flash distillation system;
43. Remove the residual alcohol present in the biofuel, reserving the same for later reuse;
44. After completion of alcohol withdrawal, switch off the low-pressure system and stop using flash distillation;
45. Add under constant stirring, the cleaning agent to initiate refining process (for this example, use the sorbent of your choice or availability on the local market as

Magnesol[®], Eco2Pure[®], Amberlite[®], Purolite[®], or another type of clay);

46. Allow interaction of the biofuel with the refining agent;
47. After the refining / cleaning agent has completed its purpose, activate the recirculation filtration system;
48. After the filter has completely removed the cleaning agent, transport the fuel fluid to a suitable container (Figure 2 vessel 14);
49. Clean the filter as necessary.

RESULTS AND DISCUSSION:

It was possible to perform three transesterification reactions, to separate three times the glycerin, to recover the excess methanol content (allowing its reuse) and to perform one operation of anhydrous refining of the fuel, among other simultaneous processes, in less than 6 hours.

Monitoring the reaction with LASER spectroscopy allowed changing the temperature of the reaction without affecting the determination of the chemical balance moment. Represented on the graph where the instrumental reading curve shows a linear behavior. Figure 4 contains comments about the different moments of the monitoring practice.

Starting the reaction at room temperature and raising the reaction's temperature during the development of the reaction contributed to energy saving, making the process more profitable. The reaction was completed even before reaching the optimum temperature for the development of the reaction. This saves time in the heating process because the reaction occurs during the heating step, rather than after heating step.

Real time LASER spectroscopy was useful for determining if there were changes happening in the chemical composition of the reaction medium and at what rate they were occurring. In the way that this experiment was carried out, Real time LASER spectroscopy is not useful to determine the concentration of the products or reagents, therefore, other techniques should be used to do it.

The monitoring time in the reactions was broad with the purpose of demonstrating the linear behavior of the reaction curve after the establishment of the chemical balance in Figure 4. The effective reaction times of the transesterification reactions are lower than the total monitoring hours.

CONCLUSIONS

The final product was obtained with the same characteristics as the one produced by traditional methods.

The reaction time was optimized with the use of an appropriate monitoring system. Monitoring of the reaction with real-time LASER spectroscopy allowed initiating the reaction at room temperature and increase the supply of energy (heat) throughout the reaction, reducing the energy consumption during the fuel production and the point of chemical balance was detected by the monitoring system in the same way as it would do if the reaction was carried out under constant temperature.

The productions costs are lower since the input of energy is lower and the production time is lower than traditional methods.

Performing the reactions near the stoichiometric limits reduced the refining time of the final product, as there is less unreacted raw material to be removed from the final product.

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CAPES, CASE 9109/11-0.

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Figure 1 – Reactor Design. Where: A = agitation system motor; B = vaccum sistem; C = filtering system; D = electroseparation system; E = blades of the agitation system; F = directional joint; G = valve; H = pump; I = flash destilation system; J = heating system; K = flash destilation system nozzle; L = Composite material

Figure 2 – General view of the process. Where: 1- Stock of oil, raw material (not used in this example); 2- Stock of cleaning agent; 3- Stock of triglycerides (fat or oil); 4- Stock of catalyzer ; 5- Stock of methanol; 6-tank for the preparation of the catalytic mixture ; 7- vacuum pump; 8- water storage tank; 9- (not used in this example); 10- (not used in this example); 11- reactor; 12 – salt container; 13- residues; 14- biodiesel container; 15- glycerin container.

Figure 3 – First reaction of transesterification monitored with LASER spectroscopy and temperature monitoring.

Figure 4 – Comments on the monitoring process on the Graph.

Figure 5 – Second reaction of transesterification monitored with LASER spectroscopy and temperature monitoring.

Figure 6 – Third reaction of transesterification monitored with LASER spectroscopy and temperature monitoring. *(In this graph the LASER was hit by the author's hand and the distortion was caused by him fixing the sensor position. The glycerin separation was not monitored.)*