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Use of Current and Potential Fluctuations Among Identical Electrodes to Determine the Induction Time of the Transesterification Reaction

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Fluctuations of potential and current generated among identical electrodes (electrochemical noise, EN) immersed in the reaction mixture of a transesterification process were used to determine the time period of the mass transfer controlled stage. The alcohol type (methanol or ethanol), and agitation speed (200, 400, and 600 rpm) were used to illustrate the potential application of EN in biodiesel development. EN has shown to be particularly valuable for determining the induction time of the transesterification reaction which is known as a stage of mass transfer control. Thin layer chromatography and thermogravimetric analysis were used to determine the chemical composition of the reaction mixture before and after the mass transfer controlled region. These results were correlated with electrochemical noise. It was demonstrated that current and potential fluctuations provide a relatively easy way to measure the elapsed time of the initial stage of mass transfer control during the transesterification process. Therefore current and potential fluctuations are a valuable tool for novel experiments during the early stages of transesterification.

Keywords: Electrochemical noise, Transesterification, Biodiesel, Induction time, Electrochemical sensor

1. INTRODUCTION

Transesterification is a reaction between vegetable oil or animal fat and a short chain alcohol (i.e. methanol or ethanol) in the presence of a catalyst to produce mono-alkyl esters (biodiesel) [1,2]. Various kinetics investigations indicate that during transesterification reaction there are three stages: first the mass transfer controlled stage, afterward one stage of kinetic control and finally the slow equilibrium stage. Most of the studies are focused on the second and third stages, which are investigated offline with a variety of spectroscopic analytical techniques [3-5]. Although these techniques offer reliability they are also time consuming, the sample treatment is complex and transportation of a reaction sample to the analytical equipment is required. The initial stage of the reaction that is controlled by mass transfer occurs in the seconds range so that make it hard to study with the spectroscopic analytical techniques. Consequently, little attention has been paid to this region. However, this initial stage has significant impact on reaction time as well as on the final biodiesel purity. Therefore the use of an electrochemical sensor that allows the determination of the induction time of transesterification reaction would be a very useful tool to study the early stage of the transesterification reaction. Knowing the induction time also would allow comparison of the agitation speed of reaction at different scales (e. g. laboratory or industrial).

One of the key features of the transesterification reaction is that the alkoxide provides aggressive ions [6] to the mixture that can cause significant fluctuation of current and potential between a pair of immersed identical electrodes (electrochemical noise, EN). The major sources of electrochemical fluctuations can be attributed to random phenomena such as: processes of adsorption and desorption, pitting and cracking, pH change, reactions controlled by activation or even mass-transfer [7]. In this method, current is measured between electrodes using a zero resistance ammeter (ZRA) and potential fluctuations are measured between these and a reference electrode or another identical working electrode. Although EN is a convenient method for monitoring the behavior of electrochemical activity primarily in corrosion studies [8,9] it could also be valuable for determining the induction time of transesterification reaction using the significant change in the mixture viscosity due to the conversion of the soybean oil to esters that in turn affect the mass transfer rate, and also change the noise signal behavior. Therefore, the aim of this paper was to demonstrate the effectiveness of current and potential fluctuations to determine the induction time of the transesterification reaction.

2. EXPERIMENTAL

2.1 Reagents

Commercial edible-grade soybean oil (Nutrioli$^{(R)}$, IndustriaRagasa, Monterrey, NL, Mexico) was purchased from a local supermarket. Reagent grade potassium hydroxide, methanol and ethanol were purchased from Fermont (Monterrey, NL, Mexico).

2.2 Transesterification

For the transesterification reaction, 20 g of soybean oil at 25 ºC were mixed with methanol or ethanol (alcohol/oil molar ratio 6:1) and 1% mass fraction of KOH relative to the oil mass. Molar weight of the soybean oil was considered to be 874 g/mol as previously reported [10,11]. The reaction was carried out in an Erlenmeyer flask under different stirring rates (600, 400 and 200 rpm).

2.3 Sensor

The electrochemical noise sensor was constructed from an aluminum alloy beverage can sheet, with an average aluminum mass content of 98% [12]. Three sheets of aluminium were embedded parallel in epoxy resin from Buehler. One of these was used as a reference electrode. The cross section (1.2 mm^2) of each aluminium electrode was exposed to the reaction mixture.

2.4 Electrochemical noise measurement

Electrochemical noise measurements were carried out with a Gamry potentiostat (PCI4/300) in the zero resistance ammeter (ZRA) mode. Both current and potential fluctuations were simultaneously recorded at a frequency of 10 Hz for 206 s. The electrochemical sensor was immersed in the oil. The beginning of the electrochemical noise test was the zero reference of the time scale. One hundred seconds from the starting point, alkoxide was added to oil and the EN measurements continued for an additional time of 106 seconds. Figure 1 shows a scheme of the experimental setup. Each experiment was repeated three times.

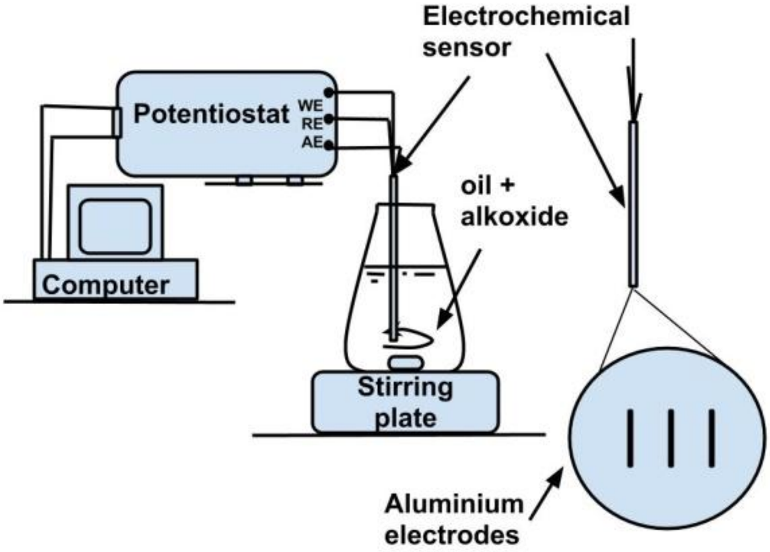

Figure 1. Sketch of the experimental setup of the transesterification process and electrochemical noise measurements.

2.5 Thin layer chromatography (TLC)

The transesterification reaction was also monitored by TLC using plastic sheets coated with silica gel 60 F (Merck). Undiluted samples of the oil/alkoxide reaction mixture were collected at 10 and 100 seconds for analysis and a sample of pure soybean oil was used as a reference. The sheets were run with a 100 mL solution of 10% ethyl acetate in hexane. For plate development a 100 mL solution of 1% KMNO4 in 4% NaOH was prepared.

2.6 Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) was performed with a thermobalance from TA instruments, discovery series. Samples were heated at a temperature scan rate of 10 °C/min, from 50 to 600 °C under a nitrogen flow of 20 cm^3 min^{-1}. Sample weights were on average 5 mg.

3. RESULTS AND DISCUSSION

3.1 Electrochemical Noise

Figure 2 shows typical behavior for current and potential fluctuations from the electrochemical sensor immersed in the transesterification reaction mixture. As can be seen in figure 2, during the first 100 seconds negligible fluctuations are observed. This is because the electrodes are immersed in a non-conductive solution (soybean oil) which also limits the mass transfer due to its high viscosity (~68 mm2/s @ 25°C). Indeed, the primary reason of the transesterification reaction is the reduction of the vegetable oil viscosity to a lower value similar to the viscosity of diesel. As seen in figure 2 the behavior of current and potential fluctuations clearly show three regions. Region I shows that after the ethoxide addition, current and potential fluctuations remain negligible during a short time, indicating that the mixture of immiscible liquids needs to wait for its homogenization to start the reaction. This initial stage is known as transesterification induction time. In region I current and potential fluctuations were similar to those obtained from the electrochemical sensor immersed in the soybean oil. This region is a mass transfer controlled stage, where vigorous agitation is needed to bring the molecules in close contact and start the reaction. Region II starts with sudden fluctuations in current and potential marking the end of region I and the beginning of the kinetically controlled stage labeled as region II. In this stage, the first mono-, and diglycerides formed increase the kinetic rate of the reaction and promote the rapid conversion of triglycerides (TG) to mono-alkyl esters [3]. A reasonable explanation for the sudden current and potential fluctuations is the presence of ions in the mixture and a reduction of its viscosity due to conversion of oil to esters. In other words, the electrodes are exposed to very different environments: during the first 100 s the electrodes are exposed to the oil, then to a mixture of two immiscible liquids (oil+alcohol) of low conductivity and high viscosity (region I), finally to monoalkyl esters with low viscosity which enhances the mass transfer and thus the electrical conduction (region II). As a result, sudden fluctuations of current and potential are observed. The last region was labeled region III and was characterized by a relatively stable current and potential signal, where residual unreacted triglyceride molecules are converted to mono-alkyl esters. In figure 2, the transesterification was carried out with ethoxide (ethanol+KOH) and the signal obtained using methoxide also shows three regions.

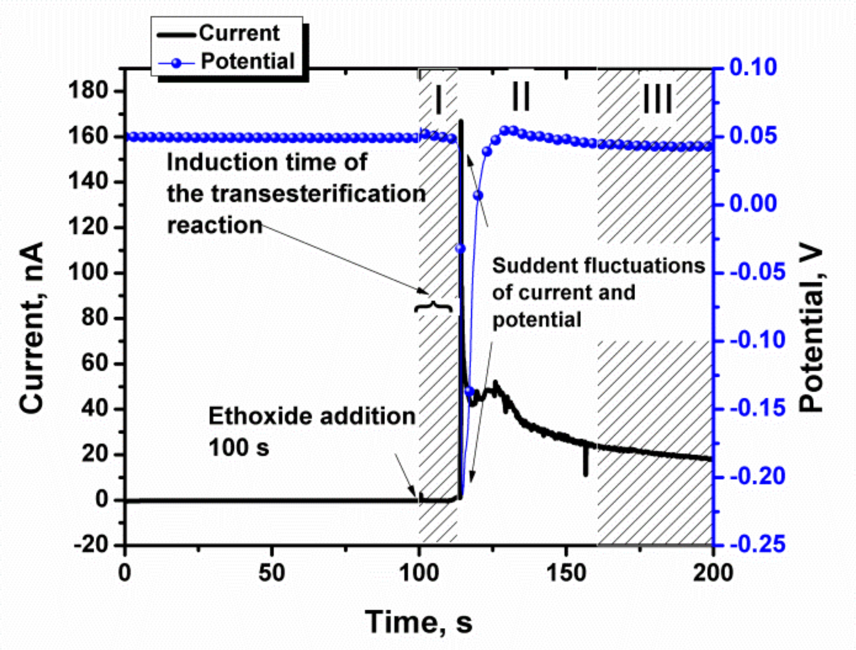

Figure 2. Current and potential fluctuations as a function of time from the electrochemical sensor immersed in the transesterification reaction mixture with ethoxide at 400 rpm

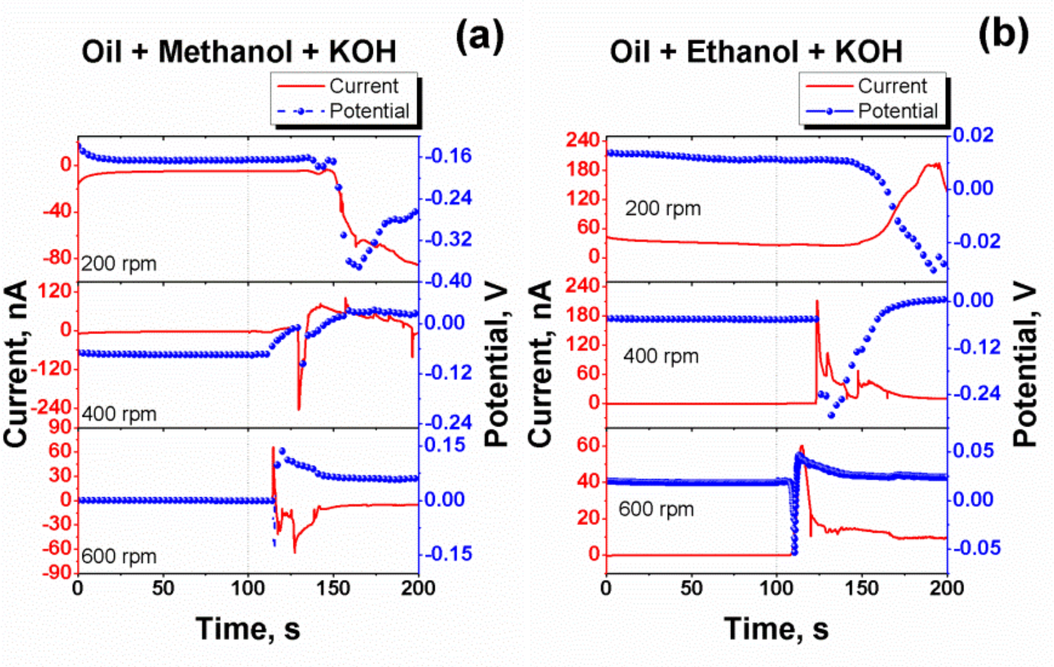

Figure 3. Current and potential fluctuations as a function of time and at different agitation speed of the transesterification reaction using a) methanol and, b) ethanol

Figure 3a shows typical behavior of current and potential fluctuations measured during the transesterification of soybean oil with methanol and potassium hydroxide at different agitation rates. Figure 3b shows similar plots but using ethanol instead of methanol in the transesterification reaction. From figures 3a and 3b it is clear that induction time depends on the alcohol type and agitation rate.

The behavior of the current and potential fluctuations is in good agreement with various kinetics studies of the transesterification reaction [13-15] that have reported an initial stage controlled by mass transfer. Table 1 shows the average values of the transesterification induction time as a function of agitation speed and alcohol type. Data in table 1 clearly shows that by increasing agitation speed the transesterification induction time decreases, as would be expected. Another important effect observed in table 1 is the low induction time obtained with ethanol compared to methanol. This result confirms that the homogenization stage using ethanol in the reaction is faster than homogenization for methanol, which coincides with the results of Stavarache [16] who found that an increase in the chain length of the alcohol also increases the miscibility between oil and alcohol. However, the miscibility when ethanol is used might not be beneficial for the separation of glycerol and esters [17].

Table 1. Transesterification induction time in seconds obtained from the current and potential time series during transesterification with methanol or ethanol as a function of the agitation rate.

Agitation rate rpm	Methanol		Ethanol	
	Induction time from current (s)	Induction time from potential (s)	Induction time from current (s)	Induction time from potential (s)
200	39.2±3	40.3±3	35.2±3	38.5±3
400	29.8±2	29.8±2	15.7±3	16.4±3
600	20.1±3	17.1±2	9.5±2	9.2±2

3.2 Thin layer chromatography (TLC) and Thermogravimetric analysis (TGA)

The average induction time was validated by comparing the composition of the reaction mixture in region I and II under an agitation speed of 600 rpm. Samples of the reaction mixture were withdrawn 10 and 100 seconds after the addition of the alkoxide and used for TLC and TGA. Figure 4a shows the thin layer chromatography results. Samples of the reaction mixture used in lane M10 and E10 were taken from region I. In the case of M10 only triglycerides are observed in agreement with the low kinetic rate due to homogenization of the reaction and also with the average induction time found for methanol at 600 rpm. On the other hand, the lane corresponding to E10 shows not only triglycerides but also a small increase in mono-, diglycerides and esters. One hundred seconds after adding methoxide or ethoxide, both samples clearly show the presence of esters. This result shows excellent agreement with those obtained by EN measurements.

Figure 4b shows TGA curves obtained upon plotting the mass loss data for a sample of the reaction mixture using methanol for the transesterification reaction. The curve (dotted-line) for the sample taken at 10 s only shows one step ascribed [18] to vegetable oil decomposition (96%). The curve (solid-line) for the sample at 100 s shows two steps, the first is ascribed to the decomposition of esters (12.4%) and the second to the decomposition of soybean oil (86%). The rest (1.6%) is due to alcohol decomposition and residual mass. These results are consistent with TLC. Figure 4c shows that after 10s (dotted-line) the composition of the reaction mixture using ethanol is approximately 14% esters and 83% soybean oil, consistent with lane E10, in figure 4a. The presence of esters is also correlated with the average induction time at 600 rpm in table 1. The curve corresponding to the sample of the reaction after 100s clearly shows an increase in esters indicating an increase in the kinetic reaction consistent with ENM.

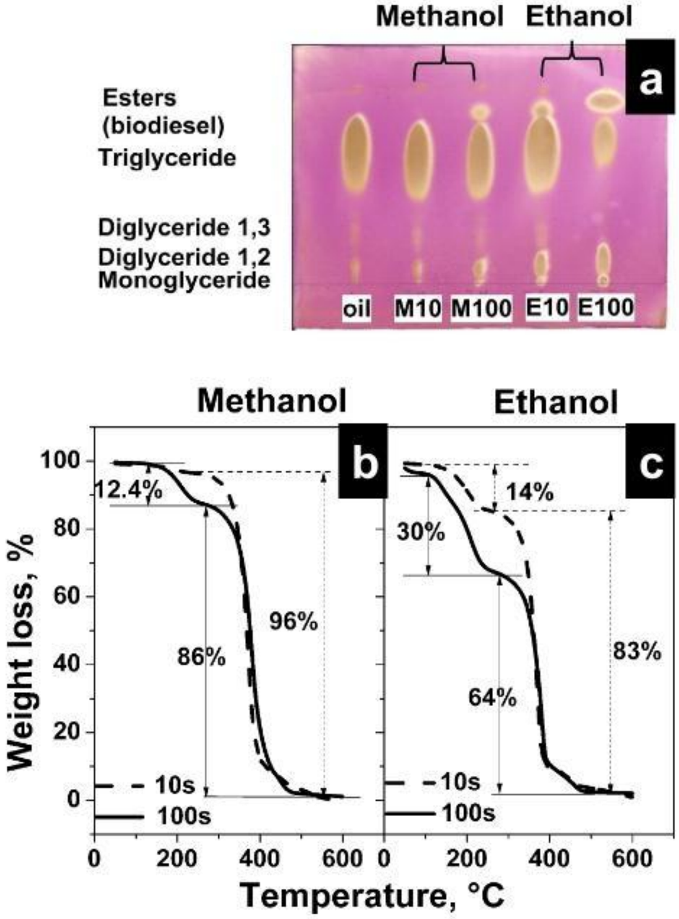

Figure 4. Thin layer chromatography a) and thermogravimetric analysis (b and c) showing the composition of the reaction mixture in region I and II using methanol or ethanol during the transesterification reaction of soybean oil. Samples were taken 10 and 100 seconds after adding alkoxide (agitation rate 600 rpm)

4. CONCLUSIONS

Based on the above results, the following conclusions can be drawn:

- The mass-transfer controlled region was clearly identified in the current and potential fluctuation plot.
- The study has proved the feasibility of the current and potential fluctuations to determine the induction time of the transesterification reaction.
- The induction time of the reaction decrease with a faster stirring decreases the induction time of the reaction.

- Homogenization of the reaction mixture with ethanol was faster than with methanol.

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References

1. H. Fukuda, A. Kondo, H. Noda, *J Biosci Bioeng*, 92 (2001) 405
2. S.P. Singh, D. Singh, *Renew Sust Energ Rev*, 14 (2010) 200
3. F. Ma, L.D. Clements, M. Hanna, *T ASAE*, (1998) 1261
4. J.A. Colucci, E.E. Borrero, F. Alape, *J Am Oil Chem Soc*, 82 (2005) 525
5. L.C. Meher, D. Vidya Sagar, S.N. Naik, *Renew Sust Energ Rev*, 10 (2006) 248
6. E. Rondero-Daniel, L.F. Díaz-Ballote, L. Maldonado-López, A. Contreras, *Rev Mex Fís S*, 55 (2009) 72
7. R.A. Cottis, *Russ J Electrochem*, 42 (2006) 497
8. Y.J. Tan, S. Bailey, B. Kinsella, *Corros Sci*, 38 (1996) 1681
9. Q. Su, K. Allahar, G. Bierwagen, *Electrochim Acta*, 53 (2008) 2825
10. W. Xie, X. Huang, H. Li, *Bioresource Technol*, 98 (2007) 936
11. W. Xie, H. Peng, L. Chen, *Appl Catal A-Gen*, 300 (2006) 67
12. G.O. Verran, U. Kurzawa, *Resour Conserv Recy*, 52 (2008) 731
13. G. Vicente, M. Martínez, J. Aracil, A. Esteban, *Ind Eng Chem Res*, 44 (2005) 5447
14. D. Darnoko, M. Cheryan, *J Am Oil Chem Soc*, 77 (2000) 1263
15. K. Gunvachai, M.G. Hassan, G. Shama, K. Hellgardt, *Process Saf Environ*, 85 (2007) 383
16. C. Stavarache, M. Vinatoru, R. Nishimura, Y. Maeda, *Ultrason Sonochem*, 12 (2005) 367
17. H. Sanli, M. Canakci, *Energ Fuel*, 22 (2008) 2713
18. P. Chand, C.V. Reddy, J.G. Verkade, T. Wang, D. Grewell, *Energ Fuel*, 23 (2009) 989