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Influence of the reaction time on the quality (physical-chemical properties) of biofuels obtained through catalytic cracking of crude palm oil

Influência do tempo de reação sobre as propriedades físico-químicas de biocombustíveis obtidos através do craqueamento térmico catalítico do óleo de palma bruto

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The present paper investigated the influence of the reaction time on the quality (physical-chemical properties) of biofuels obtained by catalytic cracking of crude palm oil (CPO). The influence of the reaction time (10, 20, 30, 40, 50, and 60 min) on the quality of crude biofuels denominated organic liquid products (OLP) was investigated through experiments carried out in a cracking pilot plant with capacity of 143 L in the following operating conditions: 20 wt% sodium carbonate (Na_2CO_3) as catalyst, 450 °C, 1 atm and batch mode operation. The quality of the biofuels produced was certified through physical-chemical analyzes (acid value, saponification value, specific gravity, refractive index, kinematic viscosity, corrosiveness to copper, and flash point). The results show that the physical-chemical properties of OLP decrease as the reaction time increases, in such a way that, catalytic cracking process occurs efficiently in the interval of 10 to 20 min after its start, which can be finalized when it reaches 30 minutes of reaction. In addition, Na_2CO_3 was essential as a catalyst in the cracking reaction to reduce the physical-chemical properties of OLPs obtained at different times, allowing the specific gravity, kinematic viscosity and corrosivity to copper to be within or very close to the limits established for Diesel S10.
Keywords: Bio-oil, organic liquid product, pilot plant.

O presente trabalho investigou a influência do tempo de reação sobre a qualidade (propriedades físico-químicas) de biocombustíveis obtidos por craqueamento térmico catalítico de óleo de palma bruto (OPB). A influência do tempo de reação (10, 20, 30, 40, 50 e 60 min) sobre a qualidade dos biocombustíveis brutos denominados produtos orgânicos líquidos (PLO) foi investigada por meio de experimentos realizados em uma planta piloto de craqueamento com capacidade de 143 L nas seguintes condições operacionais: 20% em massa de carbonato de sódio (Na_2CO_3) como catalisador, 450 °C, 1 atm e operação em batelada. A qualidade dos biocombustíveis produzidos foi certificada através de análises físico-químicas (índice de acidez, índice de saponificação, massa específica, índice de refração, viscosidade cinemática, corrosividade ao cobre e ponto de fulgor). Os resultados mostram que as propriedades físico-químicas do PLO diminuem com o aumento do tempo de reação, de forma que o processo de craqueamento catalítico ocorre de forma eficiente no intervalo de 10 a 20 min após seu início, podendo ser finalizado quando atinge 30 minutos de reação. Além disso, o Na_2CO_3 foi essencial como catalisador na reação de craqueamento para redução das propriedades físico-químicas dos PLOs obtidos em diferentes tempos, permitindo que a gravidade específica, viscosidade cinemática e corrosividade ao cobre fique dentro ou muito próximos dos limites estabelecidos para Diesel S10.
Palavras-chave: Bio-óleo, produto líquido orgânico, planta piloto.

1. INTRODUTION

Currently, fossil fuels represent the primary sources of energy that have met the energy demand of modern society. However, limited reserves of fossil fuels and global warming make their use unsustainable and cause environmental problems related to their combustion due to the emission of large amounts of CO_2 [1]. In this sense, environmentally friendly biofuels can be an alternative source of renewable and sustainable energy to meet the global energy demand for the transport sector [1, 2], which is considered the second fastest growing sector concerning energy consumption [3].

Production of biofuels that are made up of hydrocarbons can be carried out by several different routes [4]. Catalytic cracking [5-21] is one of the routes that can be applied effectively to feedstocks based on triglycerides such as vegetable oils to produce hydrocarbons [22]. Catalytic cracking of vegetable oils can generate the following products: gaseous biofuels, including hydrocarbons C1-C5, CO and CO_2; liquid biofuels, which are called bio-oil or organic liquid product (OLP); water and coke [23-26].

Several publications report the parameters that influence the catalytic cracking process of vegetable oils and the effect of these parameters on the yield and physical-chemical property values of OLP [11, 15-17, 22, 27-33]. Such parameters are temperature, reaction time, heating rate, gas flow rate, feed rate, particle size, presence of water, type of catalyst and biomass composition, among others [11, 15-17, 22, 27-33]. In parallel, the values of the physical properties of OLP are the result of its chemical composition [24], which in turn is dependent on the source of biomass and the operational conditions used in its production [28, 34, 35].

According to Chew and Bhatia (2008) [21], the temperature of the catalytic cracking process (in this case, 450°C) is lower than the pyrolysis (500-850°C). Idem et al. (1996) [36] have carried out the thermal cracking of canola oil, which was carried out in a fixed bed reactor in the presence and absence of steam, with the temperature between 300 and 500°C on atmospheric pressure, obtaining as a result a yield of 54% (w/w) into Hydrocarbons. Dandik and Aksoy (1998) [37]evaluated the residual sunflower oil conversion by thermal catalytic cracking in the presence of acid catalysts and sodium carbonate, varying the temperature between 400 and 420ºC. The results of this study showed a yield of 32.8% (w/w) of liquid hydrocarbons with the use of sodium carbonate and 420ºC. Li et al. (2009) [38] have carried out the thermal catalytic cracking of cottonseed oil in a reactor of fixed-fluidized bed and 1 atm using one zeolite as catalyst. The authors investigated the effect of temperature (400-500°C), ratio catalyst/oil (6-10) and residence time (50-90s) on the yield of gasoline and diesel fractions. The results showed that the optimal condition for thermal catalytic cracking of cottonseed oil produce the highest yield of these fractions was: reaction temperature of 426.2°C, ratio catalyst/oil of 7.8 g/g and residence time of 50.2s, getting 65.6% (w/w) of diesel fraction ($\leq$ 360°C) and 33.7% (w/w) of gasoline fraction ($\leq$ 200°C) and a minimum yield of gas equal to 11.6% (w/w).

Regarding the type of catalyst used in the catalytic cracking process, basic catalysts such as sodium carbonate (Na_2CO_3) have been investigated in order to convert triglyceride-based feedstocks into biofuels with low carboxylic acid content [7, 19, 23, 31, 36-41]. Junming et al. (2009) [42] cracked soybean oil with basic catalysts (Na_2CO_3, Al_2O_3, K_2CO_3) in the temperature range of 350 to 400 °C, obtaining biofuels with a diesel-like chemical composition, with low acid values and good cold flow properties. Weber et al. (2012) [43] performed the thermal degradation of free fatty acids and animal fat using Na_2CO_3 and 5 wt% water at 430 ± 20 °C at a pilot plant. According to the results obtained Weber et al. (2012) [41], free fatty acids yielded 64-74 wt% OLP with acid values ranging from 0.64 to 0.80 mg KOH/g, while animal fat yielded 60-70 wt% with acid values ranging from 0.5 to 1.8 mg KOH/g. Gas yields ranged from 25 to 30 wt% and coke yields from 4 to 6 wt%.

As reported above, a series of studies have been carried out on the parameters that influence the catalytic cracking process of vegetable oils, as well as their effects on the yield and quality of biofuels. However, few studies have investigated the effect of reaction time on the quality of organic liquid products. Hew et al. (2010) [15] made improvements in the OLP by catalytic cracking to mainly produce gasoline and showed that OLP yield decreases with the reaction time. In contrast, gasoline yield increases as reaction time increase from 0.5 to 15 min and decreases slightly as reaction time increases to 30 min. In parallel, as the reaction progresses, it is possible to convert more OLP into gasoline. Sousa et al. (2018) [44] performed simultaneous deoxygenation, cracking, and isomerization reactions of a fatty material with 1.5 g of the Hbeta catalyst. Operating conditions of these reactions can be summarized as follows: reaction time (5 to 10 h), temperature (300 to 350 °C), initial pressure of H_2 (10 bar) and agitation (800 rpm). According to the results obtained by Sousa et al. (2018) [44] there was a decrease in hydrocarbon content with increasing reaction time and a significant increase in gas content with increasing reaction time (68% after 7 h and 90% after 12 h), resulting in the reduction of liquid hydrocarbons.

In this context, the main objective of the present study is to investigate the influence of reaction time on the quality (physical-chemical properties) of the OLP obtained via the catalytic cracking process of crude palm oil (CPO) in a cracking pilot plant with capacity of 143 L in the following operating conditions: 20 wt% sodium carbonate (Na_2CO_3) as catalyst, 450 °C, 1 atm and batch mode operation.

2. MATERIAL AND METHODS

2.1 Crude palm oil

Crude palm oil (*Elaeis guineensis* Jacq.) was provided by Engefar Ltda (Ananindeua-Pará-Brazil). The crude palm oil (CPO) has been physical-chemically characterized as described in the literature [19]. To be used in catalytic cracking experiments, the CPO did not undergo any treatment.

2.2 Catalyst

The fresh Sodium Carbonate (Na_2CO_3), commercial soda ASH Light (D50), with a purity of 98.0 wt% were the catalysts used in this work. Solvay Chemicals International SA (Brussels, Belgium) supplied sodium carbonate.

2.3 Thermal cracking

For purposes of comparison with the results of catalytic cracking, a thermal cracking experiment was carried out on a semi-pilot scale. The methodology for this experiment consisted of weighing 785 g of CPO. Then, the CPO was introduced in a reactor made of stainless steel with mechanical agitation and a capacity of 2 L. The reactor was coupled to the semi-pilot plant, and then it was surrounded by an electrical resistance associated with a blanket made of insulating material (glass wool), in order to maintain the heating of the reaction system with the least possible loss of heat to the environment. The cracking temperature was programmed to 450ºC, with a heating rate of 10 ºC/min, under constant agitation of 750 rpm and under nitrogen flow from 0.02 ml/min to 0.04 ml/min. The vapors formed within the reaction system were condensed and collected in a collection vessel. Once obtained, the OLP was subjected to a simple filtration process to remove particulate matter (catalyst and solid waste). Subsequently, the OLP was subjected to physical-chemical analyzes, as described in Section 2.6.

2.4 Catalytic cracking

The experimental apparatus used in performing this work was a cracking pilot plant, which consists of the following systems: feed, pre-heater, sludge bed reactor, mechanical agitation (impeller), GLP burning (heating), OLP condensation, combustion gas exhaust, water recirculation and cooling, OLP collection, gas flare, and control unit. The central equipment is the sludge bed reactor of carbon stainless steel with a capacity of 143 L. Mota et al. (2014) [19] describe in detail the pilot plant used in this study.

The experimental procedure of the catalytic cracking of crude palm oil to obtain Organic Liquid Product was performed as described by da Mota et al. (2014) [19] under the following conditions: 450°C, 1 atm and 20 wt% of sodium carbonate as the catalyst. Basically, 50 kg of CPO were weighed, as well as the catalyst was weighed (20% by weight of CPO). Then, the catalyst was introduced into the reactor, while the CPO was stored in the polyethylene tank, and subsequently pumped to the sludge bed reactor, flowing through the pre-heater, in order to increase the CPO temperature to 200°C and thus be able to enter the reactor. The sludge bed reactor is heated to 450°C and the mechanical impeller was set to 150 rpm. When the reaction time of the cracking process reached 30 min, the formation of non-condensable gases was observed in the gas flare. As the amount of gases generated in the catalytic cracking reaction increases, flowing through the condenser, part of this mixture of hydrocarbons called organic liquid product was collected in a collection vessel made of stainless steel. After the reaction time of the cracking process reached 60 min, the production of the OLP was completed, as no more OLP could be collected, meaning that all the CPO has been cracked.

2.5 Evaluation of reaction time

During the experimental procedure of catalytic cracking, there was a parallel study to evaluate the influence of reaction time on the quality of OLP. Thus, the experimental procedure consists in collecting samples OLP (Figure 1) at different reaction times (10, 20, 30, 40, 50, and 60 minutes) during crude palm oil cracking. Then, the OLP samples were adequately stored in 1000 ml glass bottles and amber color. Finally, the OLP containing the mixture of all OLP obtained at different reaction times were stored in a polyethylene container of 50 L.

Figure 1: OLP samples at different reaction times.

2.6 Characterization of the OLP

OLP has been physical-chemically characterized according to AOCS and ASTM official methods for Acid Value (AOCS Cd 3d-63), Saponification Value (AOCS Cd 3-25), Specific Gravity at 20 °C (ASTM D854), Refractive Index (AOCS Cc 7-25), Kinematics Viscosity at 40 °C (ASTM 446 and ASTM D2515), Flash Point (ASTM D93), and Corrosiveness to Copper (ASTM D130).

3. RESULTS AND DISCUSSION

3.1 Thermal cracking

According to Table 1, the OLP obtained from the thermal cracking of the CPO showed high values of acidity index and kinematic viscosity. On the other hand, the values of specific mass, flash point and corrosivity to copper were within the limits established for Diesel S10, according to ANP N° 65 [45]. A more detailed analysis of the results listed in the Table 1 is presented in Section 3.2 when comparing them with the results of the catalytic cracking of CPO.

Table 1: Physical-chemical properties of the OLP obtained from the thermal cracking of CPO.

Physical-chemical properties	OLP	Diesel S10/ANP N° 65 [45]
Specific gravity at 20 °C (kg/m^3)	850	820-880
Kinematic viscosity at 40 °C (mm^2/s)	10.76	2.0–4.5
Acid value (mg KOH/g)	151.19	0.50
Saponification value (mg KOH/g)	292.11	-
Flash point (°C)	38.00	≥38
Corrosiveness to Copper. 3h at 50 °C	1A	1A

3.2. Catalytic Cracking

In Figures 2, 3, 4, and 5, the reaction time significantly influenced the values of physical-chemical properties (specific gravity, kinematic viscosity, acid value, saponification value and flash point) of the OLP during cracking crude palm oil. Through the operational conditions adopted in this study, as the reaction time increased from 0 to 60 min, these physical-chemical properties reduced sharply. This fact can be explained by the breakdown of CPO molecules due to prolonged exposure to high temperatures and the effect of the catalyst, resulting in products with lower molecular weight than CPO. Zhao et al. (2015) [11] investigated the catalytic cracking of carinata oil in a continuous flow fixed-bed reactor at 450 °C, with a nominal residence time of approximately 60 min. The results show that carinata oil was converted to hydrocarbons with molecules smaller than those of crude carinata oil, which resulted in lower density and viscosity of the biofuel. Mancio et al. (2016) [7] found that an increase in light hydrocarbon fractions caused a decrease in both the specific gravity values at 20 °C and the kinematic viscosity values.

According to Table 1, and Figures 2, 3, 4, and 5 the OLPs obtained in several times from the catalytic cracking of the CPO showed acid value and flash point values higher than that established for the Diesel S10. On the other hand, the values of specific gravity, kinematic viscosity and corrosivity to copper are within or very close to the lower limits established for Diesel S10, according to ANP N °65.

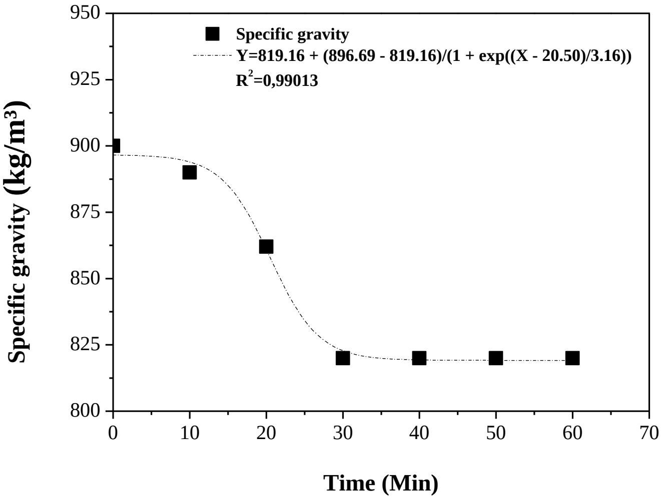

Figure 2: Specific gravity at 20 °C of OLP samples as a function of reaction time.

Figures 2, 3, 4, and 5 also show that most physical-chemical properties of OLPs significantly reduced between 10 and 30 min of cracking, remaining practically constant from 30 min. The reaction time is the primary factor to ensure a catalytic process efficiently [43]. If the reaction time exceeds the optimum time, the majority of the components present in the liquid products will further decompose into other low molecular weight products [15]. It is added to this the fact that the longer the reaction time, the higher the process cost [44].

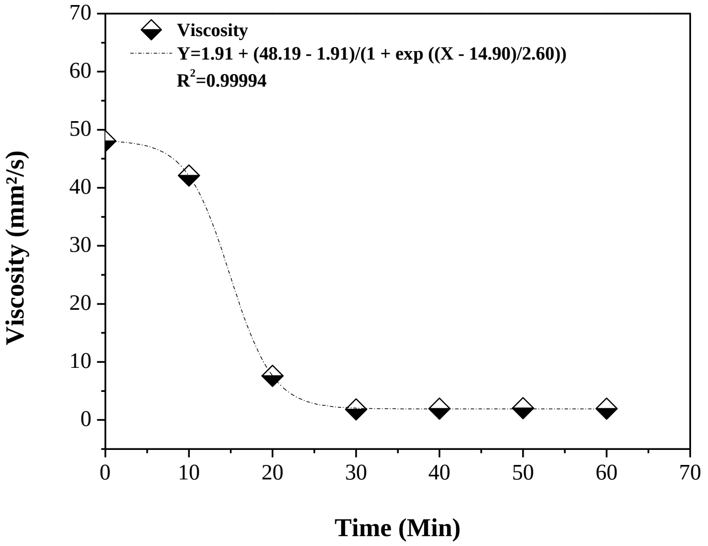

Figure 3: Kinematic viscosity at 40 °C of OLP samples as a function of reaction time.

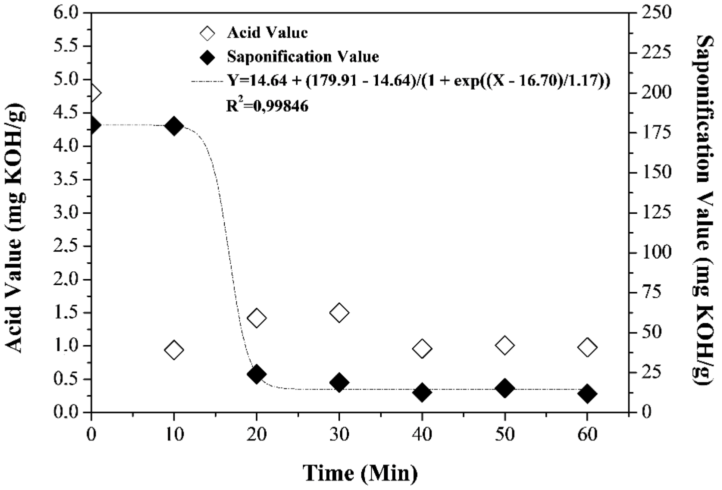

Figure 4: Acid value and saponification value of OLP samples as a function of reaction time.

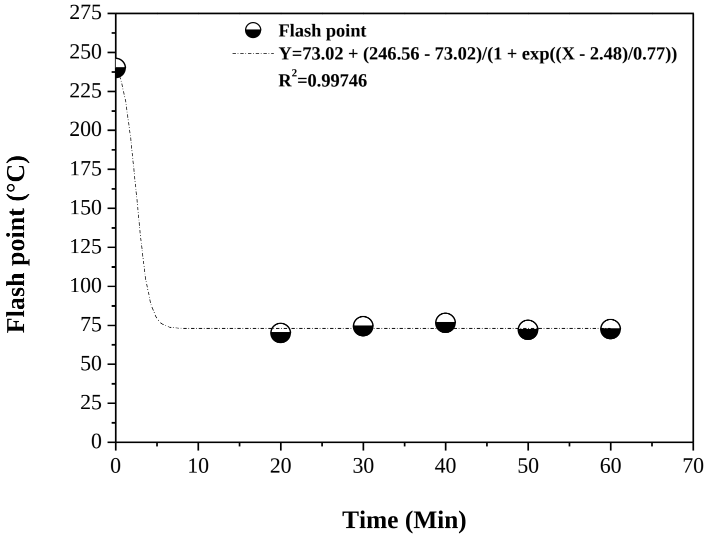

Figure 5: Flash point of OLP samples as a function of reaction time.

A more detailed analysis of Figure 4 shows that the carboxylic acids (free fatty acids) present in the crude palm oil underwent a deoxygenation process in the period of 0 to 10 min of reaction, resulting in a significant reduction of the acid value in the first 10 min. Comparing the results presented in Figure 4 for catalytic cracking with those in Table 1 for thermal cracking, the reduction in the acid value of the OLP is due to the direct and immediate influence of the use of 20 wt% of sodium carbonate. In fact, sodium carbonate has a significant effect on the deoxygenation stage of the carboxylic acids. causing a significant reduction in the content of oxygenated compounds (especially carboxylic acids) or acid phase, consequently reducing the acid value of OLP [7, 38]. Between 10 and 40 min of reaction, the values of acid value presented a small variation and did not exceed 1.5 mg KOH/g, remaining constant from 40 min. This small variation is due to the breakdown of the crude palm oil molecules and subsequently formation of compounds with predominance of carboxyls [23, 46-49]. resulting in a slight increase in the OLP acid value.

In parallel, Figure 4 also shows that in the first 10 min of reaction there was no significant change in the values of saponification value. Differently, in the period of 10 to 20 min, there was a significant reduction of the saponification value, which did not show significant alterations after 20 min of cracking. According to Canapi et al. (2005) [48], the saponification value is the number of milligrams of potassium hydroxide required to neutralize the free fatty acid and saponify the esters in one gram of fat. In other words, the saponification value informs the presence of carboxylic acids in the form of free fatty acids and bound fatty acids, i.e., in the form of esters. Therefore, we can say that there was a reaction of cracking (primary cracking followed by secondary cracking) of palm oil in the period of 10 to 20 min of reaction. promoting a significant reduction of the saponification value in that period. According to Vonghia et al. (1995) [49], Katikaneni et al. (1995) [50], Idem et al. (1996) [36], Leng et al. (1999) [51], and Taufiqurrahmi & Bhatia (2011) [23], the triglyceride molecules undergo a thermal cracking on the surface of the catalyst to form hydrocarbons and oxygenated compounds such as fatty acids, ketones, aldehydes and esters, characterizing the primary cracking. Thus, these compounds are converted by secondary cracking in gaseous products, paraffin, and olefins of long and short chains, CO, CO_2, water and alcohols, resulting in deoxygenation of oxygenated compounds, particularly, carboxylic acids.

According to Table 1 and Figure 5, for the OLP from catalytic cracking, the flash point value was higher than that established by the ANP N° 65. This fact is due to the presence of high molecular weight compounds, resulting in a value higher flash point for this OLP. The flash point indicates the presence of volatile components in the oil and is used to evaluate the overall flammability hazard of a material. The lower the flash point, the higher the concentration of light hydrocarbons in the material [52].

Table 2 shows that there were significant changes in the values of refractive index (RI) and that there were no changes in the values of corrosiveness to copper of the OLP during the 60 min of catalytic cracking. The lowest refractive index value was reached at 20 minutes of reaction, becoming a more physical-chemical property of OLP considered an indication that in the interval of 10 to 20 min there was a useful cracking reaction of CPO in molecules smaller when compared to the size of the molecules of the feedstock. According to Swern (1964) [53], one of the general relations between the refractive index and the composition of an oil-based product, with minor exceptions, is that the refractive index increases as the length of the carbon chain increases. From the 20 min of reaction, there was a gradual increase of the refractive index. without exceeding the value of the refractive index of palm CPO (RI = 1.46). as explained by da Mota et al. (2014) [19], indicating that there were at least oligomerization reactions of the products formed during the cracking process. According to Ong and Bhatia (2010) [54], light alkenes can undergo oligomerization to produce a mixture of alkenes and heavier alkanes. which are arranged under the fractions of gasoline, kerosene, and diesel.

As in the present paper, in previous works such as the work of Mancio et al. (2016) [7] and Mota et al. (2014) [19], the catalytic cracking of CPO was investigated, using sodium carbonate as a catalyst in a pilot cracking plant. However, the main difference of the present work in relation to the work of Mancio et al. (2016) [7] and da Mota et al. (2014) [19] is the study of the influence of reaction time on the physical-chemical properties of OLPs, in such a way that, from the present study it is possible to answer when the cracking reactions start, as well as the moment in which the physical-chemical properties no longer change as the cracking time progresses. Therefore, the results presented are relevant to the scientific community in the area.

Table 2: Refractive index and corrosiveness to copper of the OLP collected at different times during the catalytic cracking experiment of crude palm oil.

Physical-chemical properties	**Time (Min)**					
	10	**20**	**30**	**40**	**50**	**60**
Refractive Index	1.46	1.42	1.44	1.44	1.45	1.45
Corrosiveness to Copper, 3h at 50 °C	-	1A	1A	1A	1A	1A

4. CONCLUSION

From the present study, which investigated the influence of reaction time (10, 20, 30, 40, 50, and 60 min) on the physical-chemical properties of OLP via catalytic cracking of crude palm oil with 20 wt% Na_2CO_3 in a cracking pilot plant (143 L), it was concluded that: 1) reaction time significantly influenced the values of physical-chemical properties (specific gravity, kinematic viscosity, acid value, saponification value and flash point) of the OLP during cracking crude palm oil. As the reaction time increased from 0 to 60 min, these physical-chemical properties reduced sharply; 2) thermal catalytic cracking process occurs efficiently in the interval of 10 to 20 min after its start, which can be finalized when it reaches 30 minutes of reaction. 3) sodium carbonate was essential as a catalyst in the cracking reaction for reducing the acid value of the OLPs obtained in several times, as well as for framing the values of specific gravity, kinematic viscosity and corrosivity to copper within or very close to the lower limits established for Diesel S10.

5. ACKNOWLEDGEMENTS

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