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Transesterification Reaction of Waste Cooking Oil and Chicken Fat by Homogeneous Catalysis

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Abstract: In the last years, biodiesel production has been on a steady increase due to it is renewable and biodegradable fuel. The process to obtain biodiesel can be carried out using different raw materials. It is commonly performed by transesterification reaction of vegetable oils with methanol and using a homogeneous or heterogeneous catalyst. This work seeks to compare the results produced in transesterification of wasted cooking oil and chicken fat by homogeneous catalysis with NaOH. Due to in each case triglyceride comes from different raw materials, operation conditions differ slightly, which is more evident in the values used for the temperature. For chicken fat was used temperature variations between 35 ^{o}C and 55 ^{o}C, varying catalyst in percentages between 0.3% and 0.7% with a molar ratio 6:1 in all cases and a reaction time of 1 h. Likewise, the conditions used in the transesterification process of waste cooking oil were temperature between 50 ^{o}C and 60 ^{o}C with a molar ratio 6/1 and 9/1 for alcohol and oil, and catalyst percentage between 0.5% and 0.7% by weight. The yields obtained were between 78% and 94%, or 83% and 95%, for chicken fat and wasted cooking oil, respectively.

Key words: Biodiesel, transesterification, homogeneous catalysis, cooking oil, chicken fat.

1. Introduction

A constant diminishing in petroleum reserves is producing an increasing interest in alternative fuels to supply the demand in order to avoid increasing in the fuel price [1]. According to OECD (Organization for Economic Co-operation and Development) and FAO (Food and Agriculture Organization of the United Nations), the biodiesel production in the world is increasing steadily [2]. Biodiesel production over the last years with a prediction of the next period is presented in Fig. 1.

These data observed after 2005 have not been presented decrease in the production of biodiesel, thus projecting that for 2020 the production from 2010 will be duplicate, this is an increase of twenty billion gallons along ten years [2].

The entire world knows the environmental consequences of petroleum and gases produced by fuels derived from it [3]. By this reason, biodiesel is an alternative to diesel fuel due to it is nontoxic, renewable and biodegradable source, which can be obtained from oil produced locally, reducing dependence and increasing competitiveness to the benefit of the internal market at the same time [4]. In this way, the most recent studies have shown that the effects on the ozone layer are lower for biodiesel than for diesel, and negative effects in an aquatic ecosystem caused by the addition of diesel are more significant than for biodiesel [5].

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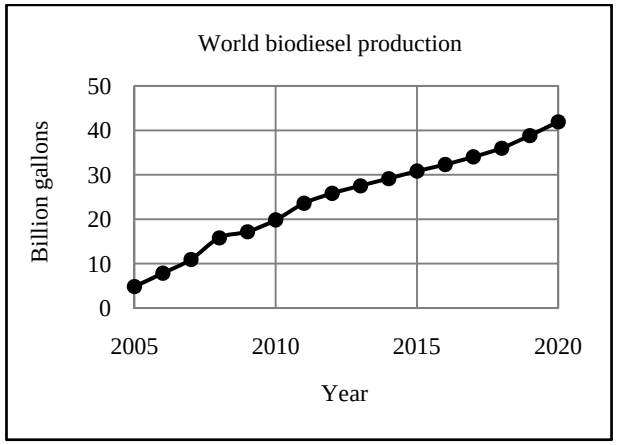

Fig. 1 Estimation of world biodiesel production.

Colombia in Latin America is starting to develop the production of renewable energy [6]. In this way, it has trebled its biodiesel production, which is mainly produced from palm oil, over a four-year period. It can be produced by any raw material that is high in triglycerides such as agricultural sources, pork lard, chicken fat and fish oil [7]. However, pork lard is not a good source for biodiesel production due to a considerable presence of stearic acids and some other fatty acids, increasing the optimum melting point of biodiesel for vehicular motors [8].

On the other hand, between 2% and 2.5% chickens mass composition are lipids and according to FENAVI (National Federation of Poultry Farmers from Colombia) every year are produced C.A one million of chickens for human consumption, that show a production around 27,000 tons of chicken fat per year [9].

Biodiesel is mainly produced by a transesterification reaction between triglycerides and alcohol in the presence of a catalyst, producing a mixture of unreacted feedstock, fatty acids esters and glycerol, which can be purified to obtain a by-product [10-13].

Methanol is mainly used to produce biodiesel used in diesel engines, it is due to their best performance and low cost, due to other types of alcohol have higher prices and these can be difficult to separate alcohol and water such as in the case of ethanol [14]. A homogeneous base catalyst such as NaOH is used to provide a high yield for suitable operation conditions. However, this type of catalyst has some problems such as its separation from products is difficult, glycerol cannot be purified when NaOH or any other homogeneous catalyst is used like catalyst, in the same way, it consumed in the reaction, so it cannot be reused or regenerated because any operation can produce cost overruns higher that catalyst price [15].

By this reason, other catalytic types such as enzymatic and heterogeneous catalysts have been studied due to they could be separated from products without complex methods, producing a decrease in production costs for reusing of the catalyst. In addition to these undesired saponification reactions from oil with high water and free fatty acids, content can be avoided by using enzymatic and heterogeneous catalyst, but this presents a mass transfer limitation, which prevents to be used for industrial applications [16].

By this reason, homogeneous catalysis is now the best way to biodiesel production, because it has the best mass transfer producing high yield by an accelerated transesterification reaction [17]. This has made it necessary to select the best feedstock to avoid problems of undesired saponification reactions with homogeneous catalysis and then carry out an optimization of the production process.

2. Feedstock Composition

Due to some problems produced by the use of edible oil to produce biodiesel, recently interest has been increased in the use of waste cooking oil to solve, at the same time, some problems of water contamination in the sewage systems [18].

Cooking oils are composed by triglycerides with a hydrophobic behavior and at the same time these are made up of three fatty acids mol, which have different number of unsaturated bonds and carbon chain length, and one mol glycerol. The most common triglycerides are composed by chains of palmitic acid, oleic acid, linoleic acid and stearic acid. When the water content

in the oil or the amount of free fatty acids is high, which is associated with waste cooking oil, is necessary to process the raw material previously to avoid the soap formation [19], this process basically consists of drying the oil and carrying out an esterification to decrease the amount of free fatty acids. When oil has a great amount of particles or impurities, it is necessary to carry out a filtration.

On the other hand, chicken fat is ever a reusable waste; it has low water and free fatty acid content and a similar fatty acids composition to waste cooking oil [17], in this case, the main components are oleic acid, palmitic acid and stearic acid [20]. The main problem with this type of feedstock is in solid state, and for this reason it needs a pretreatment to obtain small particles and then improves the mass transfer of the process.

For the development of experimental process, the waste cooking oil was collected from hotel sector, this oil has characteristics very different from edible cooking oil, the main physical differences of them are their color and the presence of particles and impurities. Density and viscosity are lower than the edible oil due to migration of water from food and a degradation of original triglycerides generating new unhealthy substances, which produce a total change in all other physical properties.

As has already been mentioned, one of the most important properties to be analyzed is the acidity of the oil, which represents the free fatty acids content. When this value is higher than 3% of oil weight, the basic transesterification cannot be performed directly over the feedstock due to soap formation. In this case, it is first necessary to carry out an esterification of free fatty acids by using an acid catalyst [21].

Another main factor to take into account is the ash percentage, which is produced by oil degradation and solid particles removed from foods fried and charred by the temperature effect. If this value is high then it is necessary to remove impurities by filtration and other methods to obtain a suitable raw material to produce a final product with low ash content, which must be lower than 0.02% of the biodiesel by mass.

Table 1 shows the main chemical and physical properties of the used cooking oil for this work. It can be seen that the feedstock has a low content of free fatty acids, ash and moisture, by this reason it is not necessary to carry out a pretreatment before transesterification.

In the same way, according to properties of chicken fat in Table 1, it has not significant impurities and water content is low. But while physical properties of waste cooking oil may has a change, chicken fat in appropriate storage conditions preserve similar properties, for this reason this raw material has an advantage over waste cooking oils, in which the amount of impurities can be high, and its moisture content varies depending to the place in which was obtained and the number of times used.

Fig. 2 shows the percentage of each type of fatty acid present in waste cooking oil (at the center) and chicken fat [14, 17]. We can see that the saturated fatty acid composition is similar in each of the raw materials used, and these have some differences in mono and polyunsaturated fatty acids composition.

Then, according to this composition, we may hope that biodiesel obtained will have favorable qualities to be used in cold climates, but a limited storage time capacity due to a high content of unsaturated acids [22].

Table 1 Chemical and physical characterization from waste cooking oil.

Characteristics	Waste cooking oil	Chicken fat
Acidity (%)	0.56	Max 0.5%
Ash (%)	0.030	0
Density 15 °C (g/mL)	0.9216	0.870
Iodine value (gI_2/100 g)	108.22	80
Peroxide value (mEq/Kg)	16.61	Max 4.0
Lovibond color	16.3 × 70.0 × 0.0	31 × 4 × 3
Moisture	0.25	0.2
Refractive index 25 °C	1.4700	
Saponification (mg KOH/g)	195.87	194.4
Unsaponifiable matter (%)	1.70	0.01
Viscosity at 37 °C (centistokes)	44.78	59.2

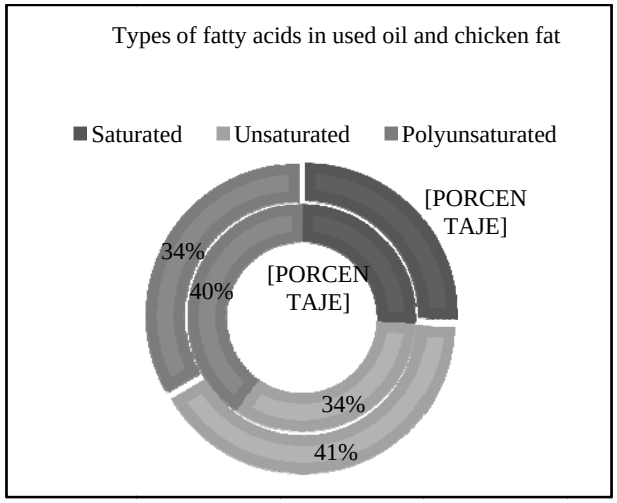

Fig. 2 Types of fatty acids in used oil (at the center) and chicken fat.

3. Biodiesel Production Process

Transesterification is the process used to obtain esters from fatty acids and triglycerides in oily sources such as chicken fat and used cooking oil. This process consists in the progressive conversion of triglycerides to diglycerides, monoglycerides and eventually glycerol by a reaction with an alcohol producing the esters [23]. Fig. 3 shows general transesterification reaction of triglycerides. Each one of these reacts with three methanol molecules to produce the same number of ester molecules and one glycerol molecule.

Due to biodiesel is obtained from fatty acids coming from triglycerides, it is composed by a mixture of fatty acid alkyl esters of alcohol used (typically methanol due to their low cost and easiness to be reused), it is known as FAME (fatty acid methyl esters) [24].

Biodiesel production process is similar with homogeneous catalysis of waste cooking oil and chicken fat. Fig. 4 shows the process for the waste cooking oil feedstock. In this case if used cooking oil has a water content higher than 0.08 wt.%, so it is necessary to carry out a dry process and then an esterification process until obtaining a weight percentage less than 3% to avoid the soap formation [25, 26]. After it the main process of biodiesel production can be carried out using a homogeneous catalyst, which is the transesterication process showed in Fig. 3.

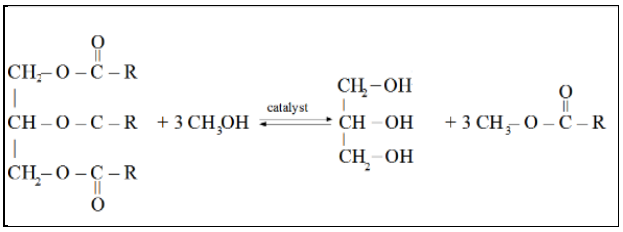

Fig. 3 Transesterification reaction.

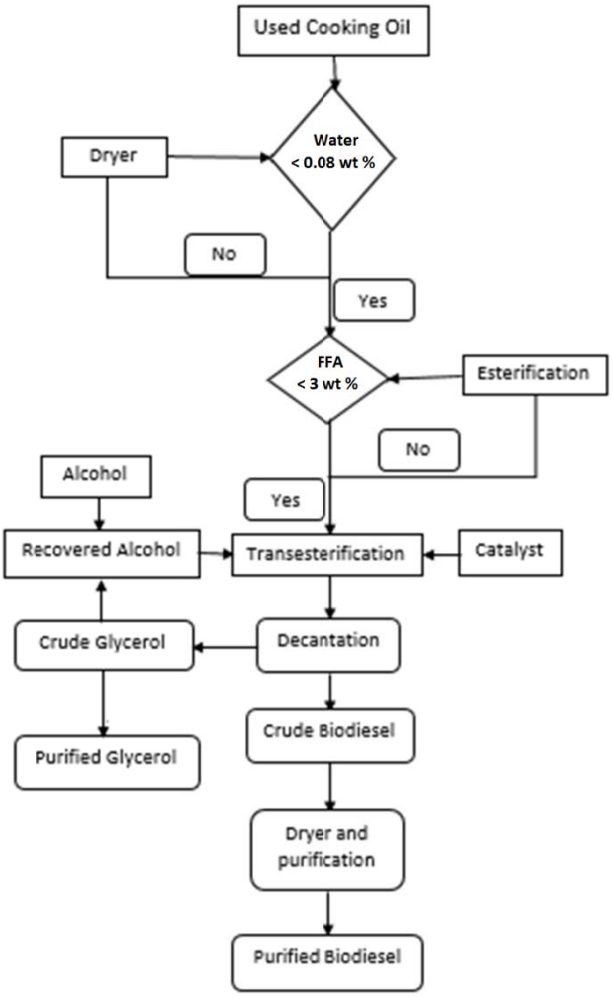

Fig. 4 Biodiesel production process.

After biodiesel production process is necessary carry out a phase's separation to obtain both an organic phase and an aqueous phase, the first have a high content of esters, the second content formed glycerol, methanol and catalyst. Glycerol obtained as by-product is hard to be purified due to a high content of catalyst, and now many lines of researches are trying to reuse it as a final product or a feedstock to another production process [27].

On the other hand, for chicken fat the purification process is not necessary due to it has a few content of water and free fatty acids, but due to it is in solid state, it is necessary to carry out a breaking down to obtain small particles to improve the mass transfer and to reduce the reaction time. After that is necessary to continue with separation and purification process (Fig. 4). Then biodiesel produced is purified by distillation removing its little methanol content [28].

4. Experimental Process

The experimental process was carried out using appropriate conditions for each system according to the feedstock used, for e.g, chicken fat was used a molar ratio alcohol/oil of 9/1, temperature between 35 °C and 55 °C, and a catalyst amount between 0.3% and 0.7%, while for waste cooking oil was used two temperature levels 50 °C and 60 °C, and a catalyst amount of 0.5% and 0.7%, and using an alcohol/oil molar ratio of 6/1 and 9/1. Conditions for transesterification process are showed in Table 2.

In the case of waste cooking oil, molar ratio was selected taking into account that for a higher ratio than 9/1 the separation of methyl ester from glycerol is more difficult and there is a neglected change in the same way for a lower ratio the fatty acids conversion is not complete. By the same reasons were selected the molar ratio 6/1 for chicken fat.

However, temperature values were selected taking into account that for lower temperatures the yield was affected negatively and for higher values the oil is burned and the reaction is not completed. To define the percentage of catalyst was selected the maximum value of 0.7 wt.% at which yield was not affected.

Sodium hydroxide was used as a catalyst because it is one of the most used in homogeneous catalysis due to its low price and good results. So by using this catalyst we have a reference point to improve both oleaginous feedstock and best operating conditions.

To assure a full interaction between all selected operating conditions for chicken fat were necessary to carry out nine tests and for the waste cooking oil were necessary eight tests. These samples were identified by a code as shown in Tables 3 and 4 to distinguish them from each other and facilitate data management.

Table 2 Condition for transesterification process.

Chicken fat		Waste cooking oil		
T (°C)	Catalyst (%)	*T* (°C)	Catalyst (%)	Molar ratio
35	0.3	50	0.5	6/1
45	0.5	60	0.7	9/1
55	0.7			

Table 3 Yield for transesterification of chicken fat.

Code	*T* (°C)	Catalyst (%)	Yield (%)
BUCO11	35	0.300	93.95
BUCO12	35	0.500	93.98
BUCO13	35	0.700	93.88
BUCO21	45	0.300	93.53
BUCO22	45	0.500	93.63
BUCO23	45	0.700	93.74
BUCO31	55	0.300	93.92
BUCO32	55	0.500	93.92
BUCO33	55	0.700	93.15

Table 4 Yield for conversion of waste cooking oil.

Code	Molar ratio	Catalyst (%)	*T* (°C)	Yield (%)
BCF111	6/1	0.5	50	88.034
BCF112	6/1	0.5	60	94.588
BCF121	6/1	0.7	50	93.474
BCF122	6/1	0.7	60	85.676
BCF211	9/1	0.5	50	93.496
BCF212	9/1	0.5	60	89.974
BCF221	9/1	0.7	50	94.755
BCF222	9/1	0.7	60	92.998

5. Results and Discussion

5.1 Gas Chromatography and Mass Spectrometry

To determine the final composition from each obtained biodiesel samples was used an analytical process known as gas chromatography coupled to mass spectrometer. This process consists in the sequential separation of each components of the mixture that in this case is a methyl esters mix with few traces of catalyst, methanol, glycerol and fatty acids. Then we can know which fraction of the raw material is turned into biodiesel and thus to know the yield of the reaction in order to establish the optimal conditions of the process.

By gas chromatography analysis is obtained a chromatogram for each biodiesel sample as is shown in Fig. 5, it shows the result obtained from experiment with used cooking oil identified by code BUCO11. On this chart we can identify each of the mixture components represented by a peak with retention time against abundance of each one.

Thus by a simple correlation between the areas for each one peak is possible to know the proportion of each methyl ester in the final product and relate them with original triglycerides in the oil, it is necessary to know the proportion of these which was transformed into biodiesel. Tables 3 and 4 show the results obtained for each sample in terms of yield for chicken fat and waste cooking oil, respectively.

5.2 Data Analysis

The program Design Expert 7.0 was used to obtain a response surface of experimental yield collected data. For chicken fat, temperature and percentage of catalyst were introduced as a continuous numeric variable, and molar ratio was added to it in the case of waste cooking oil.

To establish a correlation between the selected variables and the yield obtained, data were processed according to the model that is the best assimilated to them. Figs. 6 and 7 show the response surface to chicken fat and waste cooking oil, respectively. Temperature is given in Celsius degrees and catalyst percentage was calculated over total weight. Alcohol/oil molar ratio was the only dimensionless variable due to it is a relation with the same measure units.

In the first case, it is observed that for low temperatures a change in the amount of catalyst does not produce appreciable changes in the yield while with an increase of temperature, a variation in the proportion of catalyst is most meaningful.

On the other hand, for waste cooking oil we can observe two different behaviors depending on the alcohol and waste cooking oil ratio. When the ratio was 6:1, the yield behavior varies significantly depending on each of the variables, in this case, it is observed that for 50 ^{o}C an increase in the amount of catalyst produces higher yield, while for 60 ^{o}C the yield decreases with the increase in the amount of catalyst used. At the same way for a molar ratio of 9:1, lower temperatures and a higher amount of catalyst produce better results. Thus, better yield is observed for 50 ^{o}C and 0.7% catalyst, while the worst result was obtained at 60 ^{o}C and 0.5% catalyst.

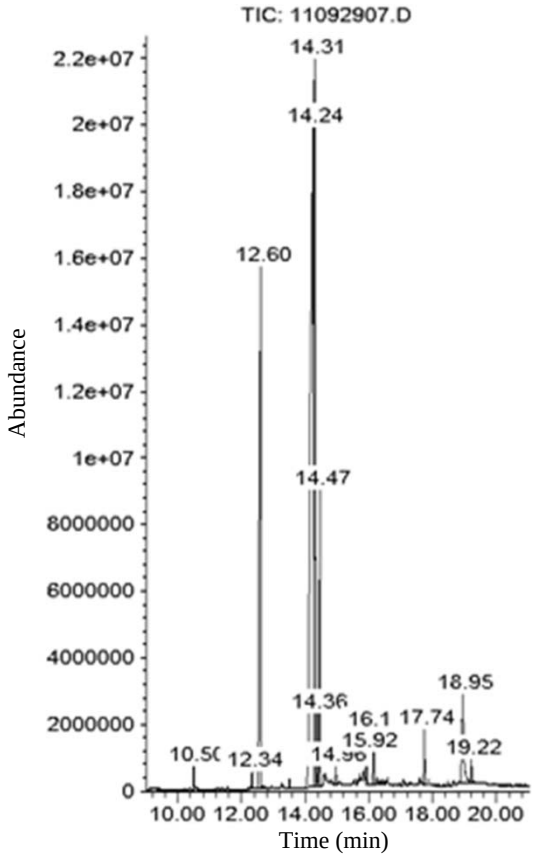

Fig. 5 Chromatogram for experiment BUCO11.

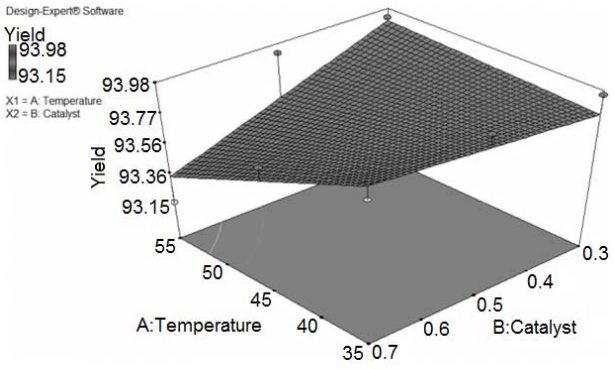

Fig. 6 Chicken fat response surface.

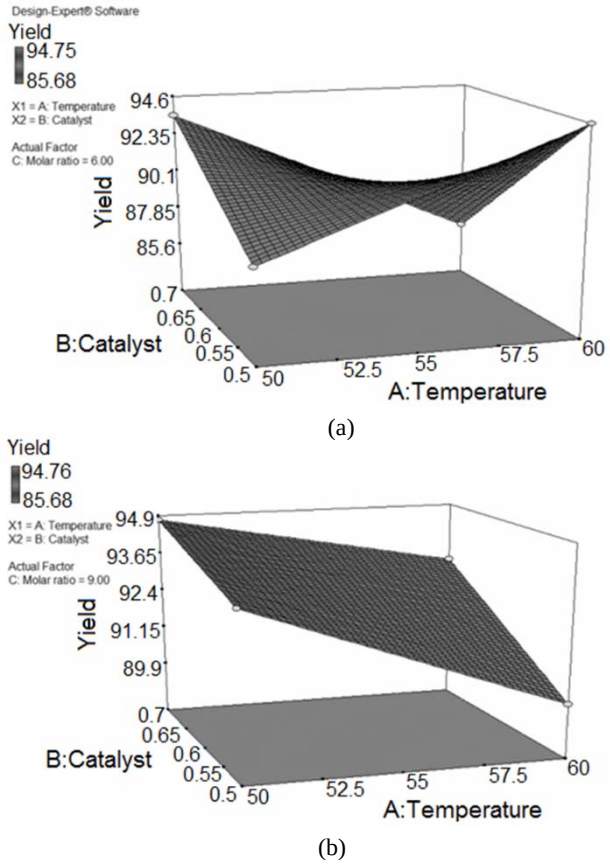

Fig. 7 Response surface used cooking oil, (a) molar ratio = 6:1, alcohol:oil, (b) molar ratio = 9:1, alcohol:oil.

6. Conclusions

Biodiesel is the best alternative as substitute for fossil fuel and it has better environmental properties due it is a biodegradable, renewable and non-toxic fuel.

According to the data, the best conditions for obtaining biodiesel from chicken fat and waste cooking oil are 35 ^{o}C and 0.3% catalyst and 50 ^{o}C, 0.7% catalyst and molar ratio 6:1, respectively.

Temperature for chicken fat is 15 ^{o}C lower than the same for waste cooking oil and percentage of catalyst is also greater when this raw material is used.

Due to the availability of the raw material, the most used process is using waste cooking oil. Chicken fat would be used, but it would not be sufficient to meet the entire demand, but it represents a significant proportion of actual biodiesel production.

For this reason and due to its low cost is expected that waste cooking oil would be the most important feedstock for biodiesel production replacing at the same time the other edible and non-edible oils.

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