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Transformation of Palm Oil over H_3PO_4 / SiO_2 Catalysts

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ABSTRACT

This paper presents the results obtained in the catalytic cracking of palm oil using phosphoric acid in different percentages (12, 24 and 30% w/w) impregnated on silica. The reaction products were analyzed by gas chromatography, infrared spectrometry, nuclear magnetic resonance and as the acid value. The acidic and textural properties of the catalysts were obtained by analyzes of adsorption/desorption of N2 (BET method), temperature programmed desorption of NH3 (NH3 TPD) and total acidity by Hammett indicators.

Keywords : Palm Oil, Cracking, Phosphoric Acid, Silica, Biofuel.

I. INTRODUCTION

The study of the conversion of vegetable oils through thermal and/or catalytic cracking can be used as a promising possibility to obtain alternative chemicals and liquid fuels, where the selectivity of the reaction products is strongly influenced by the nature of the catalysts.

The main constituents of vegetable oils are fatty acid triglycerides which can be decomposed by cracking into a mixture of saturated hydrocarbons, unsaturated aromatic hydrocarbons, ketones, aldehydes and carboxylic acids. The selectivity of these reactions depends on the catalyst being used. In order to generate a mixture of hydrocarbons with carbon chains similar to those of diesel and/or gasoline, the ideal is to select catalysts with properties that favour the reaction of decarboxylation and/or hydrodeoxygenation [1-5].

The objective of this work was to study the cracking reaction of palm oil using phosphoric acid catalysts supported on silica and check its efficiency in biofuel production process. The catalytic system H_3PO_4/SiO_2 had been previously tested by the authors [6] in soybean oil cracking with very promising results. For the present study, two processes were evaluated: thermal cracking of crude palm oil and catalytic reforming of this product obtained from the thermal cracking. The catalysts were characterized in order to correlate their activities with their textural and acidic properties. The reaction products were evaluated by acidity measurements, gas chromatography, infrared spectroscopy and ^{13}C NMR.

In relation to emissions, the absence of sulfur in vegetable oil makes the product derived from it more appropriate than the petroleum derivatives. In addition, the cracking has great applicability in places requiring lower production volume and having lower availability of skilled labor.

II. METHODS AND MATERIAL

Preparation of Catalysts

H_3PO_4/SiO_2 catalysts were prepared by impregnation of silica with phosphoric acid solution (wet point method). The silica support was dried in an oven at 383K for 12h, cooled in a desiccator to room temperature for the impregnation of phosphoric acid solution. The amounts of H_3PO_4 loadings were 12, 24 and 30% wt%. After impregnation, the catalyst was dried in an oven at 383K for about 12 hours.

BET Surface Area and Pore Size Distribution

The BET surface area, pore volume and average pore diameter were calculated from N_2 adsorption / desorption isotherms at liquid N_2 temperature (77K), using a surface area and pore size analyzer ASAP 2000 from Micromeritics. The pore size distribution was obtained from the desorption isotherm, using the BJH model. Before measurements, the samples were degassed at 473K for 16 hours in N_2 gas flow to remove physisorbed water.

Temperature Programmed Desorption of Ammonia (NH_3 TPD)

This technique was used to investigate the surface acidity characteristics of the supported materials. Analyzes were performed in a multipurpose unit with a thermal conductivity detector and the amount of sample used was approximately 0.2 g. Initially, the samples were pretreated at 623 K, and the He gas flow rate of 30 mL min^{-1} for 1 hour. The procedure was then the adsorption of ammonia (2.91% NH_3/He, 30 ml min^{-1}) at 423K. In sequence, desorption was monitored using a heating rate of 2.5 K min^{-1} to final temperature of 723K.

Total Acidity from Hammett Method

The catalyst previously dried was placed in contact with a non-aqueous solvent (heptane) and then a Hammett indicator was added to this prepared suspension. Subsequently, the sample was titrated with n-butylamine until restoration of the basic colour of the indicator. The titrant volume consumption is used to estimate the total acidity of the sample.

Catalytic test

This process was conducted in two stages, both in a batch reactor. First stage: thermal cracking of crude palm oil at 623K, for 5 hours (aiming to carboxylic acid formation). Second stage: 20g of the product obtained from first stage was subjected to reform reaction in the presence of 5 g of catalyst at 623K during 1 hour (aiming to hydrocarbon formation). The reaction products were analyzed by gas chromatography, acidity index, infrared spectroscopy and 13C NMR.

Gas chromatography analysis

The products distribution was obtained by gas chromatography using a HP 5890 series II Model equipment, using a fused silica capillary column and H_2 as carrier gas. The oven temperature was programmed from 313K to 543K in a total of 60 min of analysis.

Acidity index (AI)

The obtained product was diluted in cyclohexane and titrated with a 0.1 M KOH in ethanolic solution, using phenolphthalein as the indicator. The acidity index of the sample is calculated by the number of mmols of KOH consumed in the titration.

Infrared Spectroscopy

The analysis of the reaction products was evaluated qualitatively by Fourier transform infrared (FTIR) using a Perkin Elmer Spectrum One equipment in the wavenumber region of 4000-450 cm^{-1}.

Carbon Nuclear Magnetic Resonance ^{13}C NMR

Carbon Nuclear Magnetic Resonance ^{13}C NMR spectra were recorded on a Varian 300 MHz instrument and reported in ppm relative to deuterochloroform (77.23 ppm).

III. RESULT AND DISCUSSION

A. Specific surface area and total acidity

The textural properties of the solid materials (support and H_3PO_4/SiO_2 catalysts) obtained by the BET method and the total acidity obtained by the Hammett method are given in Table I.

TABLE I

TEXTURAL PROPERTIES OF THE CATALYSTS

Catalyst	**S_g ($m^2\,g^{-1}$)**	**V_p ($cm^3\,g^{-1}$)**	**D_p (Å)**	**Total Acidity (mmol g^{-1})**
SiO_2 (support)	274	0.060	74	0.03
12% H_3PO_4/SiO_2	220	0.058	78	1.11
24% H_3PO_4/SiO_2	202	0.068	62	2.23

Sg Specific surface area; Vp Pore volume; Dp *Pore diameter*

From Table I, it is observed that the impregnation with phosphoric acid caused a reduction in the specific surface area, probably due to the increase of the average pore size (12%) and to a partial pore blockage caused by the incorporation of the acid (24%). Furthermore, the increased content of H_3PO_4 favoured the total acidity of the solid.

B. Temperature Programmed Desorption of Ammonia (NH_3-TPD)

NH_3-TPD profiles for the different materials prepared are shown in Figure 1. The distribution obtained for all samples exhibits a single maximum desorption peak at around 473-523K, indicating that the acid sites have only weak acid strength. There was a shift, though very small, of the maximum NH_3 desorption temperature to higher values and an increase in peak intensity with the introduction of higher levels of phosphoric acid, suggesting that an increment in phosphoric acid concentration increased the acid site density.

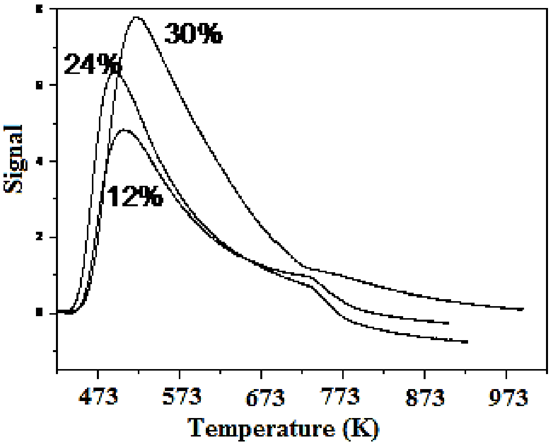


Figure 1 : Temperature Programmed Desorption of Ammonia (NH3-TPD) profiles for different catalysts.

C. Cracking Process

In order to obtain a raw material with reproducible characteristics, thermal cracking of crude palm oil was accompanied by measuring the variation of the acidity index with time. It was found that after 5 hours at 623K in the cracking batch reactor at reflux, the acidity index remained almost constant at 37.3 mg KOH/g sample. Thus, this product was used as a raw material for all the catalytic tests.

The liquid product obtained in the thermal cracking with pure silica had an acidity index of 83.8 mg KOH/g sample, indicating the formation of a large amount of fatty acids. However, impregnating the support with a moderate Brönsted acid caused a decrease by more than 25% in the acid value, due to formation of products other than fatty acids for the samples impregnated with phosphoric acid. These results are summarized in Table II where the AI values represent the medium results obtained from at least two reactions for each catalyst.

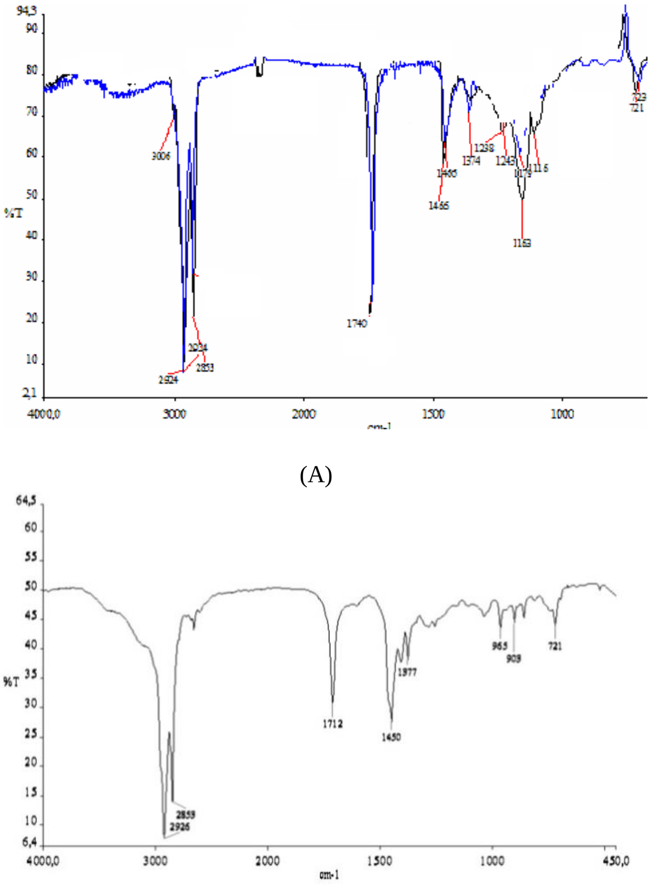
TABLE II
ACIDITY INDEX (AI) OF THE CRUDE OIL, THE RAW MATERIAL (CRACKED OIL) AND THE CATALYTIC CRACKING PRODUCTS.

Sample	AI
Crude oil	7.5
Cracked oil	37.3
SiO_2	83.8
12% HP/SiO_2	61.8
24% HP/SiO_2	69.8
30% HP/SiO_2	76.9

The infrared spectroscopy allows checking the transformation of the palm oil by detecting the characteristic bands of the functional groups. Vegetable oils are composed of esters of higher fatty acids (triglycerides) that may be in saturated or unsaturated forms. The esters have two characteristic absorption bands from the axial C=O (1750- 1735 cm^{-1}) and C-O (1300-1100 cm^{-1}) deformations.

A comparison of the infrared spectra corresponding to crude palm oil and its products after the catalytic cracking is showed in Figure 2. It indicates changes in the oil structure with the disappearance of the ester characteristic bands. On the other hand, a strong band appeared around 1712 cm^{-1} characteristic of the presence of saturated carboxylic acid. No C=O absorptions stretch were observed at 1725 cm^{-1} and 1720 cm^{-1} indicating the absence of aldehyde or ketone. Furthermore, in comparison with the crude palm oil, there was the appearance of a band at around 1450 cm^{-1}, which can be attributed to the presence of the CH_2 group.

The results of NMR ^{13}C also indicates, by the absence of signals in the 180 ppm region characteristic of the carboxyl group, that compounds like aldehydes and ketones were not formed (Figure 3). The ^{13}C NMR spectra also confirms the free fatty acid presence observed by the signal at 24.73 ppm that corresponds to CH_2 radical at ß position related to carboxyl group.



(A)

(B)

Figure 2: IR spectra: (A) - Crude palm oil; (B) – Product of the catalytic cracking using 12% HP/SiO_2 catalyst.

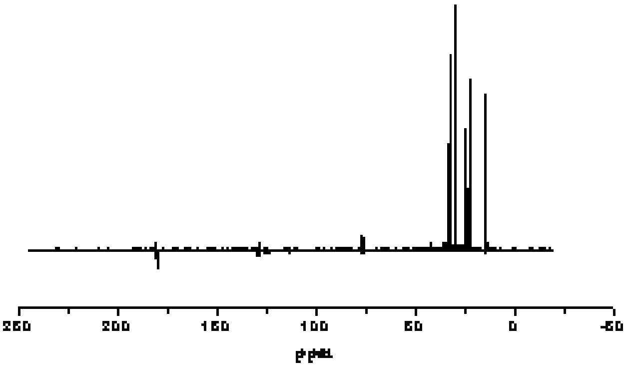


Figure 3: NMR ^{13}C spectrum for 12% HP/SiO_2 catalyst

The analysis of the liquid product indicates that it consists of free fatty acid and hydrocarbon mixture. The distribution of hydrocarbons obtained by gas chromatography analysis is presented in Table III.

TABLE III
CARBON CHAIN PRODUCT DISTRIBUTION OBTAINED BY GAS CHROMATOGRAPHY (C_X INDICATES THE NUMBER OF CARBON ATOMS IN THE MOLECULE).

Carbon chain	**SiO_2**	**12% HP/SiO_2**	**24% HP/SiO_2**	**30% HP/SiO_2**
C_5-C_{12}	15.04	12.04	4.67	9.16
C_{13}-C_{18}	47.82	33.60	36.07	41.44
>C_{18}	37.12	54.36	59.28	49.37

From Table III, it is observed that pure silica favoured the formation of hydrocarbons in the C_{13}-C_{18} range. On the other hand, catalysts impregnated with phosphoric acid favoured the formation of products derived from the polymerization reaction in the C_{18}-C_{24} range. The generation of these high molecular weight compounds, which must have already been produced in the first step of the process, caused partial blocking of the catalyst, impairing thereby the second process step.

Taking into account only the product distribution, the compounds in the C_{18} to C_{24} range could be used as biolubricants, while the compounds in the C_5-C_{12} and C_{13}-C_{18} ranges could be used as substitutes for gasoline and diesel oil, respectively. Therefore, the acidity of the catalyst (and/or the specific area) may be used as a criterion to drive the reaction to the desired product.

IV. CONCLUSION

A catalyst prepared by impregnating a moderate Brönsted acid over the silica support generated a mixture of hydrocarbons and fatty acids from the catalytic reforming of palm oil. The values of the acidity index for these products exceed those of the thermally cracked oil. Aldehydes or ketones, usual products obtained from vegetable oils degradation reaction, were identified, neither by infrared spectroscopy nor by ^{13}C NMR.

The chromatography results showed some variation of the carbon chain product distribution. Silica was more selective in products with carbon chain of C_{13} to C_{18}, which have a structure similar to diesel. On the other hand, the use of H_3PO_4/SiO_2 catalysts led to products with a carbon chain greater than C_{18} regardless of the concentration of H_3PO_4 used.

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