

**PREPARATION AND CHARACTERIZATION
OF ACTIVATED CARBON/Cu CATALYST
BY ELECTROLESS COPPER PLATING
TO OBTAIN FATTY ALCOHOLS**

**JUAN F. GONZALEZ, LILIANA GIRALDO
and J. C. MORENO-PIRAJÁN**

Departamento de Ingeniería Química
Facultad de Ingeniería
Universidad de Los Andes
Colombia

Departamento de Química
Facultad de Ciencias
Universidad Nacional de Colombia
Colombia

Departamento de Química
Facultad de Ciencias
Grupo de Investigación en Sólidos Porosos y Calorimetría
Colombia
e-mail: jumoreno@uniandes.edu.co

Abstract

The catalytic synthesis of fatty alcohols from oil palm over activated carbons (ACs)/Cu prepared by electroless copper plating has been studied. It is found that copper content on carbon surfaces increased with increasing plating time. However, a slightly gradual decrease of adsorption properties as electroless plating time increases, including specific surface areas and total micropore

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volumes based on D-R and *t*-plot approaches, is observed within the range of well developed micropore structures. The experimental results showed that, the net heat of adsorption or BET's C of the ACM/Cu samples is largely influenced by the amount of copper metal. Consequently, the catalytic ability of ACM/Cu samples for synthesized is dependent on the copper content, adsorption properties of the specimens, and the reaction time on stream.

1. Introduction

As supply of fossil fuel is limited whilst energy demand continues to rise, hence alternative renewable fuels have received increasing attention for future utilization. In this respect, fermentation, transesterification and pyrolysis of biomass, industrial and domestic wastes have been proposed as alternative solutions for the increasing of energy demand and environmental awareness [1, 2, 14, 16-20, 24, 25, 27-29]. Among these different approaches, transesterification seems to be a simple and an efficient method for fuel production. Transesterification is the chemical reaction between triglycerides and short-chain alcohol in the presence of catalyst to produce mono-ester. The long-and branched-chain triglyceride molecules are transformed to mono-esters and glycerin [4-6, 9, 10]. Commonly-used short-chain alcohols are methanol, ethanol, propanol, and butanol. Methanol is used commercially because of its low price [10]. The overall transesterification reaction can be shown by the following reaction equation in Figure 1, where R1, R2, and R3 are long hydrocarbon chains, sometimes called fatty acid chains.

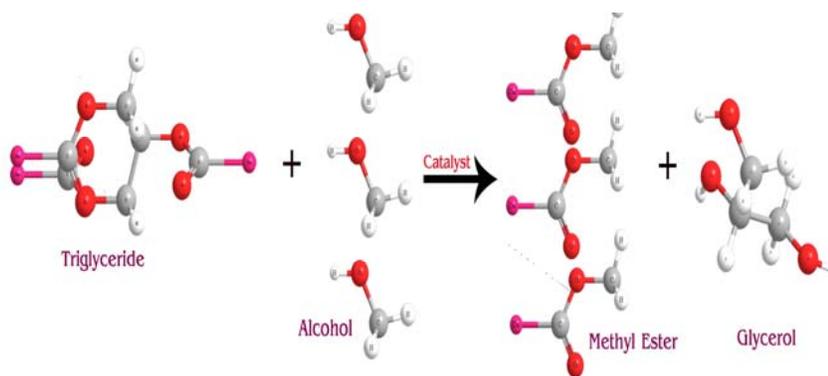


Figure1. The overall transesterification reaction equation.

There are only five chains that are most common in vegetable oils and animal fats (others are present in small amounts) [11, 12, 21]. In transesterification, triglycerides in vegetable oils or animal fats react with alcohol to form a mixture of glycerol and fatty acid alkyl esters, called biodiesel (BD) [1]. Another advantage is decreasing in viscosity of vegetable oils, and improvement of fuel properties of product fatty acid alkyl esters in the process of transesterification. Because, the viscosity of vegetable oils is much higher than that of diesel, if vegetable oils were directly used in diesel engines, they would present several related problems. The process of transesterification makes BD usable as fuel in current compression ignition (CI) engines. BD has higher oxygen content than petroleum diesel, and it shows great reductions in carbon, emission of particulate matter, monoxide, polyaromatics, sulphur, hydrocarbons, smoke, and noise [9]. In spite of the favorable effect on the environment, the economic aspect of BD production is likely to be a barrier for its development due to the fact that most of the BD produced is from edible oil, only few researches have been done for producing BD from non-edible and cheap oils. Use of edible oil as biodiesel resource costs about 60-70% of raw material cost [27].

Nevertheless, nowadays, the hydrogenation of the methyl esters is importance in presence of a catalyst to obtain the respective fatty alcohols; these are very important in the chemical industry of the tensoactives and detergents between others. Attention has recently been focused on supported Ni-Cu bimetallic catalysts due to their potential application in this process type. The reaction which is carried out at strong reaction conditions. It was determined that the ratio of nickel to copper on the catalyst [16, 24, 29], the nature of the support [17-19, 29], and the catalyst particle size [19] affect both the activity and selectivity of supported bimetallic catalysts. The potential of various Ni-Cu / γ -Al₂O₃ catalysts, which had been prepared according to different impregnation sequences of γ - alumina was evaluated in the process of hydrogenation of alkyl esters product of transesterification of palm oil. Although, the Ni-Cu / γ -Al₂O₃ catalysts have been studied by different characterization methods [14, 18, 20, 27, 28]. However, economic use of metal with catalysts, where porous solids with high surface area can be an

interesting alternative to produce fatty alcohols. This work presents a new method for synthesized fatty alcohols, from catalyst electroless copper plating on activated carbon monoliths using as raw material oil palm.

2. Experimental

2.1. Preparation of carbon monolith

The monoliths were prepared by pressing for 5MPa to a temperature of 423.15K in a uniaxial press built in our laboratory, Figure 2. The carbon monolith samples were made from bituminous coal as binder tar of petroleum. The final form of monoliths is 5mm in thickness and 12mm in diameter, respectively.

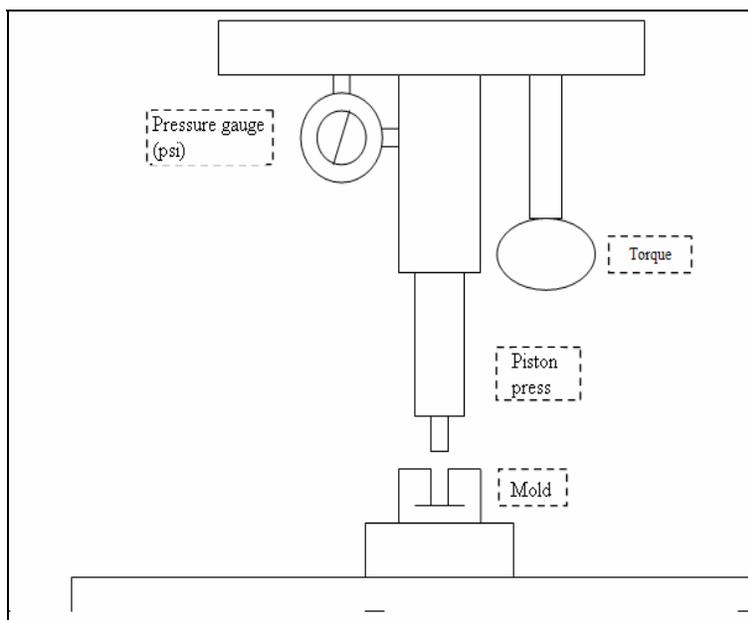


Figure 2. Uniaxial press for obtaining activated carbon monoliths honey comb.

The coal was ground and sieved for synthesis using a particle size of $20\mu\text{M}$. It was impregnated with a desiccant agent, in this case, tar of petroleum (1 wt%) for 12 hour at 373K followed by drying at 383K for about 2 hours. After this, it was put in axial press, Figure 2, at varying pressure levels; pressing at 423K formed the molding, obtaining honey comb using of mold correspond.

These structures were carbonized in an oven at a temperature of 723K, at N_2 flow of 85mL/min and warming at $1^\circ\text{C}/\text{min}$ for 2 hours, Figure 3. Finally, samples were washed with hydrochloric acid 0.1M and distilled water to neutral pH to eliminate the remains of the chemicals agent used in the impregnation.

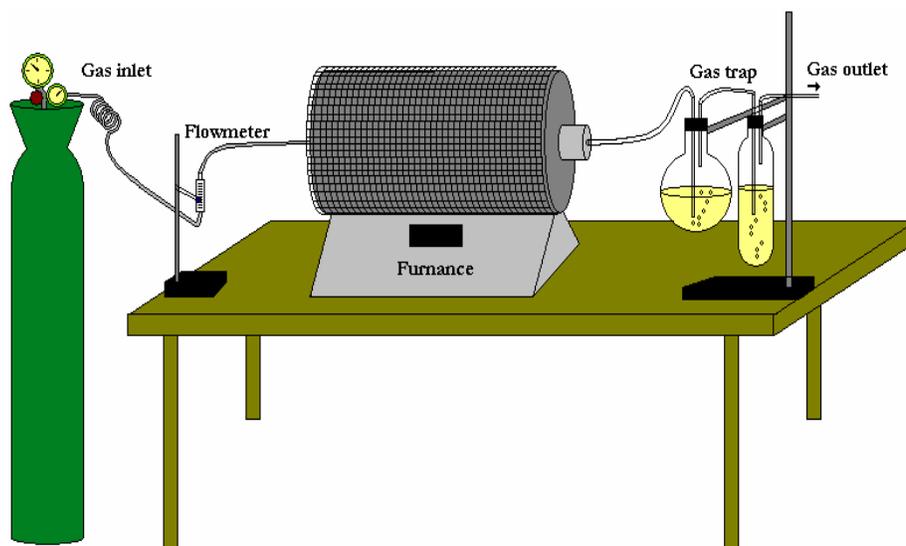


Figure 3. Assembly in the laboratory to synthesize activated carbon monoliths.

2.2. Materials and sample preparation

The activated carbon monoliths were synthesized under condition reported by us. To sensitize the surface of carbon, activated carbons were immersed in a solution composed of acidified tin chloride solution at a concentration of 1g/L for 20min at 290K, and followed by a rinse with distilled water. Prior to electroless copper plating, the activated carbons

were immersed in an aqueous solution containing palladium in ppb for 2min at 298K to maximize the autocatalysis. A palladium loaded activated carbon is introduced into the copper plating solution consisting of a 1.0:2.50:1.31 mole ratio of CuSO_4 :EDTA Na_2 :HCHO with different plating times at 318K [7].

2.3. Adsorption measurements

The surface structural characteristics of carbon monoliths were determined from N_2 (77K) adsorption isotherms results (AUTOSORB 3B Quantachrome). The surface area (S_{BET}) of carbon monolith was calculated by analyzing N_2 adsorption data with the Brunauer-Emmett-Teller (BET) theory (relative pressure range: 0.01-0.05). The micropore volume (V_0) were obtained by Dubinin-Raduskevich equation, and the total volume of porous (V_{T}) was evaluated from the nitrogen adsorption data at a relative pressure range of 0.99 by Gurvistsch rule. The mesopore volume (V_{mes}) was determined by using the Barrett-Joyner-Halenda (BJH) equation. By knowing the BET surface area (S_{BET}) and total pore volume (V_{T}), the average pore width was calculated by using the following expression, ($4V_{\text{T}}/S_{\text{BET}}$). The porosity development and available void volume were analyzed by using a field emission scanning electron microscope JEOL JSM 6510(SEM) (Japan). A SEM image of the adsorbent can be observed in the Figure 4. The channels are regulars with side length between (453 and 532) μm , while the channel walls have a thickness between (367-387) μm . Additionally, the identification and amount of copper on the activated carbons were evaluated by energy dispersive X-ray analysis (EDX, Hitachi, S-2460N), and inductively coupled plasma (ICP, AtomsScan 25, Thermo Jarrell Ash Co.), respectively.

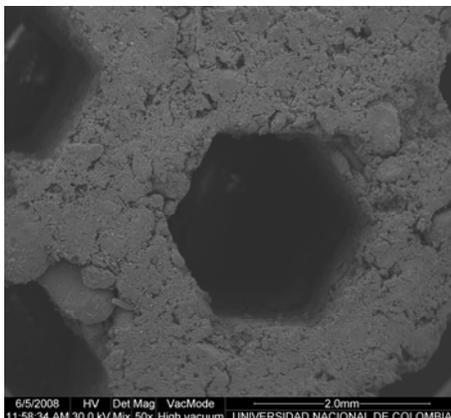


Figure 4. Morphology of the activated carbon honeycomb monolith.

2.4. Synthesis of methyl esters (biodiesel)

Transesterification reactions were carried out in 500mL flask equipped with a reflux condenser. The reactor was filled with 200g crude palm oil. The catalyst, potassium hydroxide was dissolved in methanol, and then added to the reactor. The mixture was heated to selected temperature. After the end of the reaction, the mixture was cooled to room temperature and transferred to a separatory funnel. The two layers were separated by sedimentation. The methyl ester phase was washed with hot distilled water. The excess methanol was removed on a rotary evaporator at atmospheric pressure. Drying the solution over anhydrous sodium sulphate and filtering. The biodiesel product was analyzed for its purity by using HPLC, after measuring the production weight. The methyl ester yield was defined as follows.

Methyl ester yield (%) = Production yield (%) × Methyl ester concentration (wt/wt).

2.5. Hydrogenation of methyl esters (biodiesel) with the catalyst

The catalytic capacity of the bimetallic catalyst synthesized was evaluated from a series of hydrogenation processes by using oil palm to 10 atmospheres of pressure and a temperature 453K. The hydrogenation was made by Parr Company a Shaker Type Hydrogenation Apparatus equipment series 3916. The level of activity of each one was evaluated by

base in the consumption of hydrogen. The colloidal catalyst and 65mL butan-1-ol were fed into the reactor. Hydrogen gas was charged several times to replace air, and the catalyst was activated for 120min with vigorous stirring. After the palm oil (1% w/w) was injected, the reaction was started. The hydrogen consumption was monitored with a graduated gas burette. The reaction was stopped after 120min. The partially hydrogenated palm oil were sampled at different intervals and analyzed by GC-MS for determine the conversion to fatty alcohols [11, 12, 21].

3. Results and Discussion

Figure 5 shows the well-identified EDX spectrum of a ACMCu-60 sample of activated carbon electroless-plated with copper metal. The content of copper on activated carbon monoliths increased linearly by increasing the plating time, as seen in Table 1.

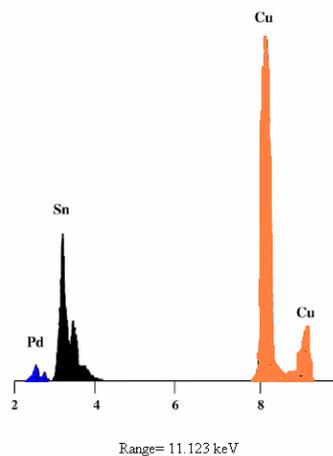


Figure 5. EDX spectra of catalyst ACMCu-60 with copper deposited through electroless plating.

The BET surface areas of activated carbons gradually decreased with increasing time of electroless copper plating, within the range of well developed micropore structures ($> 989\text{m}^2/\text{g}$), as seen in Table 1. The decrease in surface area is a result probably of partial blocking of micropores on the carbon.

This means that the amount of copper on the activated carbons can be controlled by regulating the electroless plating time in an aqueous solution containing copper precursors and reducing agent with ease. While, it is well known that one of the useful methods for the adsorption behavior of simple organic compounds on porous solids is the classical Dubinin-Radushkevich (D-R) expression for volume-filling of micropores [8, 13, 23, 26].

Table 1. Nitrogen data and copper content for activated carbon electroless-plated with copper

Sample	$S_{\text{BET}}^a (\text{m}^2 \cdot \text{g}^{-1})$	$t_v^b (\text{cm}^3 \cdot \text{g}^{-1})$	D-R $_v^c (\text{cm}^3 \cdot \text{g}^{-1})$	BET "C"	$\Delta E_d (\text{kJ} \cdot \text{mol}^{-1})$	Copper content (wt%)
ACM-original	1245	0.62	0.59	546	3.98	0
ACMCu-10	1100	0.57	0.55	564	4.06	2.0
ACMCu-20	1045	0.53	0.50	578	4.10	4.6
ACMCu-40	997	0.49	0.45	600	4.14	7.9
ACMCu-60	989	0.45	0.42	1900	4.88	10.7

^a Specific surface area determined from BET method.

^b Total micropore volumes determined from t -plot method.

^c Total micropore volumes determined from D-R plot.

^d Net heat of adsorption calculated from BET "C".

$$\frac{W}{W_0} = \exp\left(-\frac{A}{\beta \cdot E}\right)^2,$$

where $A = RT \ln(P_0/P)$ is the differential free energy of adsorption, W is the volume of liquid-like adsorbate present in the micropores at temperature T , and relative pressure P/P_0 , W_0 is the total micropore volume, β is the affinity coefficient, and E is the characteristic free energy for the adsorption depending on the system. Table 1 shows that, the total micropore volumes of activated carbons monoliths determined by D-R plot [8] and t -plot [15, 22] of nitrogen adsorption, decreased with increasing time of electroless plating. The net heat of adsorption ($\Delta E = E_0 - E_L$) derived from BET's C (C_{BET}) can be calculated as follows [9, 10]:

$$C_{BET} = \exp\left(\frac{E_0 - E_L}{RT}\right),$$

where E_0 and E_L are the heat of adsorption in the first layer and the heat of liquefaction, respectively, R is the gas constant, and T is the Kelvin temperature. Therefore, the difference between heat of adsorption and the heat of liquefaction (ΔE) is the net heat of adsorption or excess heat of adsorption in the first layer. It is surprising that, the net heat of adsorption (ΔE) or adsorption potential of AC/Cu increased with increasing plating time, within the range of well-developed micropore volumes (17) even though, the C_{BET} volumes are high, and they increased with increasing plating time. It is noted that the resulting adsorption behavior at very low relative pressures ($P/P_0 < 0.05$) is influenced by the electroless plating of copper on activated carbon, even though, the BET surface areas gradually decrease as the plating time increases. The pore size of activated carbons decreased with increasing plating time, as seen in Figure 6 [11].

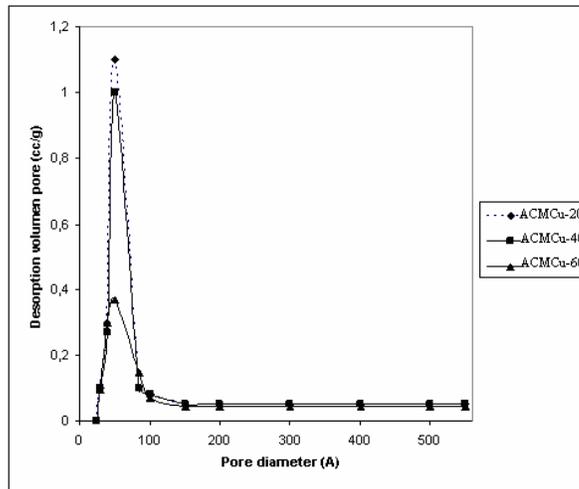


Figure 6. Pore size distribution activated carbon monoliths calculated the N_2 adsorption at 77K.

This seems to be a consequence of increased blocking of micropores on the carbon, as the plating time increased. The catalytic effect of the activated carbon monoliths surface treated with electroless copper plating for obtained fatty alcohols from oil palm is shown in Figure 7. The experimental results showed that, all of the samples prepared by electroless copper plating led to higher transesterification of oil palm for synthesized the alcohols than that of unplated one. In the presence of O_2 , the higher the content of copper on the activated carbon monoliths, the higher is the conversion, until about 60 hrs of reaction time on stream.

In Figure 7, it shows the results for the synthesis of fatty alcohols using each of the catalysts with major wt% of copper on activated carbon monoliths synthesized in this work. It is noted that the highest yield is obtained for all catalyst ACM-Cu, but the yield for the catalysts ACMCu-20, ACMCu-40, and ACMCu-60 was about 80% higher than the percentage reported in the literature.

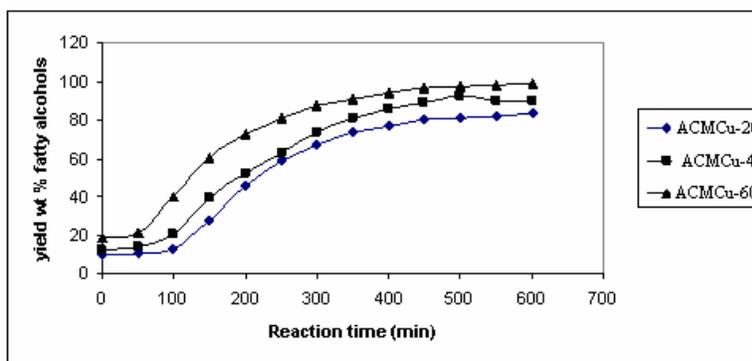


Figure 7. Fatty alcohols production with synthesized catalyst ACMCu-20, ACMCu-40, and ACMCu-60.

These results show that a greater amount of copper on the carbon permits greater efficiency in the production of fatty alcohols from products of palm oil transesterification.

While, in the cases of ACMCu-40 and ACMCu-60, fatty alcohols synthesis show a very similar pattern with the reaction time on stream,

in spite of the difference in their copper content on activated carbons. The reason for this unexpected result can be attributed to the resulting behaviors that the surface and adsorption properties of ACMCu-40, including BET surface areas and total micropore volumes, are higher than those of ACMCu-60, although, the copper content and the net heat of adsorption (or BET's *C*) are lower. The amount of fatty alcohols by ACM/Cu samples is largely influenced by the copper content, the net heat of adsorption on the surface, adsorption properties of the samples, and the reaction time on stream in this system. From the results above, the state of metallic copper is changed into copper oxides resulting in high fatty alcohols conversion from oil palm.

Conclusion

The specific surface areas and total micropore volumes of ACM/Cu samples gradually decreased as the electroless copper plating time increased. This is a consequence of an increase in the partial blocking of micropores on the carbon. However, the copper content and the net heat of adsorption increased with increasing plating time, resulting in improving the fatty alcohols yield as the reaction time on stream increased. The copper metal deposited on the activated carbons monoliths increases the ability of synthesized fatty alcohols from oil palm by the catalytic reactions of oil palm-Cu and ACM-Cu. It is clearly found here that, ACMCu-40 is a very prominent catalyst for obtained fatty alcohols in this system, and it is concluded that electroless copper plating on activated carbons is a useful method in the preparation of the ACM/Cu catalysts for synthesized fatty alcohols.

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