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Research Article

Nanotechnology Role for the Production of Clean Fuel E-85 and Petrochemical Raw Materials

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There have been a number of substantive technical changes that can be described as revolutionary process and evolutionary process. One of these approaches is the use of nanotechnology in the two-stage pyrolysis of petroleum residues of the heavy distillates separated from the Arabian crude oil. Two-stage catalytic pyrolysis technique proved to be an excellent method for the production of unsaturated hydrocarbons (which easily can be converted to alcohol, by addition of H_2O, for the production of E-85, i.e., clean fuel) regardless the type of feed stocks used. Basically, the catalysts are arranged into three large groups; amorphous and crystalline alumino-silicates, alkaline or alkaline earth alumino compounds, and different metal oxides on different catalyst carriers such as Zeolites. The high yield of ethylene (30–40%) brought by different catalysts at temperatures of 700–750°C appear to justify the intensive research work in this field.

1. Introduction

Upgrading of heavy ends for the manufacture of olefins is the main aim of the refineries today. Production of fuel-grade distillate from petroleum residues is a profitable operation for refineries provided that they have necessary technology available. Any processing to convert heavy ends into refined distillates should somewhere include a hydrogen addition step, heteroatom removal step. However, in the two-stage pyrolysis technique, the feed stock can be used without any pretreatment [1–8], regardless of the type of the feed stock used (contaminants are left as pyrolysis residue at the first stage) and the pyrolyzate as then contains high percentage of ethylene and propylene (≈37 wt. % unsaturated) using the normal catalyst. However, when we used the nanocatalyst in the two-stage pyrolysis technique, the unsaturated hydrocarbons reaches ≈85 wt. % in the pyrolyzate yield (i.e., the creative technology is the best protection against uncertainties of the future). Nowadays, scientists do their best to find new sources for clean energy (as the uses of alcohol as it is or as a blend with gasoline 15 vol. % to form E-85).

2. Aim of the Present Work

Obtain unsaturated hydrocarbons from petroleum residues with the help of different types of nanocatalyst and computer program to optimize the pyrolysis parameters of the two-stage reactor.

3. Experimental

An experimental study has been carried out of the effectiveness of some catalysts on the yield and product distribution of the two-stage pyrolysis process. Two topics are discussed.

The first topic is the effectiveness of CaO catalyst on the yield and product distribution of the two-stage pyrolysis of

gas-oil, with the intention of the producing ethylene and propylene.

The second topic deals with the two-stage catalytic pyrolysis of light distillates separated from Egyptian crude using nanocatalyst. These catalysts were prepared by different shapes.

Bimetallic colloids can be prepared by simultaneous reduction of two kinds of metal ions with or without the protecting agent or by successive reduction of one metal nuclei of the other.

4. Materials

(A) The feed-stock fraction is the gas-oil supplied by Cairo-Petroleum-Refining and used as it is without pretreatment.

(B) The (CaO) catalyst used has been supplied by "Union Carbide"—Tarrytown Technical Center—and composed of Ca^{++} (30-511) Lot number 3358-16, however, the gold nanocatalyst supported on the CaO catalyst and used as powder was supplied by "National Institute Laser Science" (NILES).

5. Procedure

The pyrolysis has been carried out using a batch-type apparatus. A quartz reactor tube (22 mm, 12 mm I'd) was placed horizontally through two separate electric furnaces, and the temperature was controlled by adjusting the electric current of the heaters. Quartz boat containing 0.2 gm of the feed-stock (Gas-Oil) with 1.5 gm of nickel sheet was inserted into the lower -temperature zone with the help of a quartz tube through which argon gas was allowed to flow. The cracked oil and gases produced at the first stage (200–400°C ±5°C) were carried to the second stage (325–500°C ±5°C) by the argon gas to undergo subsequent pyrolysis under the influence of the catalysts bed used.

A fixed catalyst bed was placed in the second stage by packing the catalyst in layers supported by a quartz wool plug. After a lapse of certain reaction time, the quartz boat is removed, cooled, and weighed to determine the amount of the pyrolyzed residue. The produced gases were collected in a gas burette. The optimum contact tine of the first stage from different experiments was found to be 15 min (the contact time of the feed-stock with the nickel catalyst in the first stage, low-temperature reaction zone). The second stage contact time varied (2.6–3.4 sec).

The pyrolyzate hydrocarbons were analyzed using Gas Chromatography (GC-mass): Agilent 6890 plus Gas chromatograph under the following conditions:

Detector: FID 250°C

Injector: split 1 : 20 250°C, 0.5 mL

Carrier: Ar 3 mL/min.

5°C/min

Oven: 50 → 200.

6. Result and Discussion

The influence of the first stage temperature (T_1) in the distribution of hydrocarbon pyrolyzate using gold (Au) nanoparticles as spheres supported on (Cao) catalyst has been illustrated in Figure 1, and the mathematical expressions for the yield of unsaturated hydrocarbons were given for each of the following:

$$\begin{aligned} Y\ \text{ethylene} &= -4e^{-7}(T_1)^4 + 0.0005(T_1)^3 \\ &\quad - 0.2(T_1)^2 + 34.367(T_1) - 2169.1, \\ Y\ \text{propylene} &= -4e^{-9}(T_1)^5 + 6e^{-6}(T_1)^4 \\ &\quad - 0.0034(T_1)^3 + 0.9037(T_1)^2 \\ &\quad - 117.27(T_1) + 5916, \\ Y\ \text{total-unsaturated} &= -5e^{-7}(T_1)^4 + 0.0005(T_1)^3 \\ &\quad - 0.2225(T_1)^2 + 40.974(T_1) \\ &\quad - 2677.3. \end{aligned} \tag{1}$$

The influence of the second stage temperature (T_2) on the distribution of hydrocarbon pyrolyzate using the gold (Au) nanoparticles as spheres supported on the CaO catalyst has been illustrated in Figure 2, and the mathematical expressions for the yield of unsaturated hydrocarbons were given for each of the following:

$$\begin{aligned} Y\ \text{ethylene} &= 1e^{-6}(T_2)^4 - 0.0017(T_2)^3 \\ &\quad + 0.9937(T_2)^2 - 253.68(T_2) + 24348, \\ Y\ \text{propylene} &= -1e^{-6}(T_2)^3 + 0.0012(T_2)^2 \\ &\quad - 0.4054(T_2) + 43.027, \\ Y\ \text{total-unsaturated} &= 1e^{-6}(T_2)^4 - 0.0018(T_2)^3 \\ &\quad + 1.0424(T_2)^2 - 279.97(T_2) + 26788. \end{aligned} \tag{2}$$

The influence of the first stage contact time ($\boldsymbol{\tau}_1$) on the distribution of hydrocarbon pyrolyzate using the gold (Au) nanoparticles as spheres supported on the CaO catalyst has been illustrated in Figure 3, and the mathematical expressions for the yield of unsaturated hydrocarbons were given for each of the following:

$$\begin{aligned} Y\ \text{ethylene} &= -0.011(\boldsymbol{\tau}_1)^4 + 0.615(\boldsymbol{\tau}_1)^3 \\ &\quad - 11.578(\boldsymbol{\tau}_1)^2 + 87.74(\boldsymbol{\tau}_1) - 175.55, \end{aligned}$$

$$Y\ \text{propylene} = 0.0116(\tau_1)^3 - 0.557(\tau_1)^2 + 7.887(\tau_1) - 26.976,$$
$$Y\ \text{total-unsaturated} = -0.011(\tau_1)^4 + 0.6034(\tau_1)^3 - 11.69(\tau_1)^2 + 92.239(\tau_1) - 193.94. \quad (3)$$

The influence of the second stage contact time (τ_2) on the distribution of hydrocarbon pyrolyzate using the gold (Au) nanoparticles as spheres supported on the CaO catalyst has been illustrated in Figure 4, and the mathematical expressions for the yield of unsaturated hydrocarbons were given for each of the following:

$$Y\ \text{ethylene} = 7492.2(\tau_2)^4 - 90324(\tau_2)^3 + 407054(\tau_2)^2 - 812743(\tau_2) + 60662,$$
$$Y\ \text{propylene} = 111.09(\tau_2)^3 - 1057.5(\tau_2)^2 + 3338(\tau_2) - 3491.6, \quad (4)$$
$$Y\ \text{total-unsaturated} = 9068.2(\tau_2)^4 - 109393(\tau_2)^3 + 493322(\tau_2)^2 - 985682(\tau_2) + 736288.$$

The influence of the catalyst to oil (r) ratio on the distribution of hydrocarbons pyrolyzate using the gold (Au) nanoparticles as spheres supported on the CaO catalyst has been illustrated in Figure 5, and the mathematical expressions for the yield of unsaturated hydrocarbons were given for each of the following:

$$Y\ \text{ethylene} = -0.072(r)4 + 2.9078(r)^3 - 39.63(r)^2 + 205.94(r) - 300.35,$$
$$Y\ \text{propylene} = -0.0089(r)^4 + 0.3664(r)^3 - 4.9547(r)^2 + 25.432(r) - 34.671,$$
$$Y\ \text{total unsaturated} = -0.0769(r)^4 + 3.1102(r)^3 - 42.123(r)^2 + 218.53(r) - 311.88. \quad (5)$$

Studying the effect of shape of the gold (Au) between (rods, prisms, and spheres) [9–20] nanoparticles supported on CaO catalyst on the distribution of hydrocarbon pyrolyzate produced from two-stage catalytic pyrolysis of the feed stock fraction separated from Egyptian crude oil under the same optimum conditions at which the maximum yield of unsaturated hydrocarbons produced from two-stage catalytic pyrolysis of feed stock fraction using Au-nanoparticles; $T_1 = 200^\circ$C, $T_2 = 400^\circ$C, $\tau_1 = 10$ min., $\tau_2 = 3$ sec., cat/oil ratio (r) = 1 : 15, it was found that the rod shape nanoparticles have the highest catalytic activity than nanoprisms and nanospheres, that may be due to the presence of different crystalline facets (110) which is absent in nanoshheres and nanoprisms, this facet has higher catalytic properties than others and give the highest yield for total unsaturated hydrocarbons (85.22 wt. %), mainly ethylene (79.41 wt. %) and propylene (5.8 wt. %), while the total unsaturated hydrocarbons using nanoprisms yield 62.28 wt. %, mainly ethylene (51.75 wt. %), and propylene

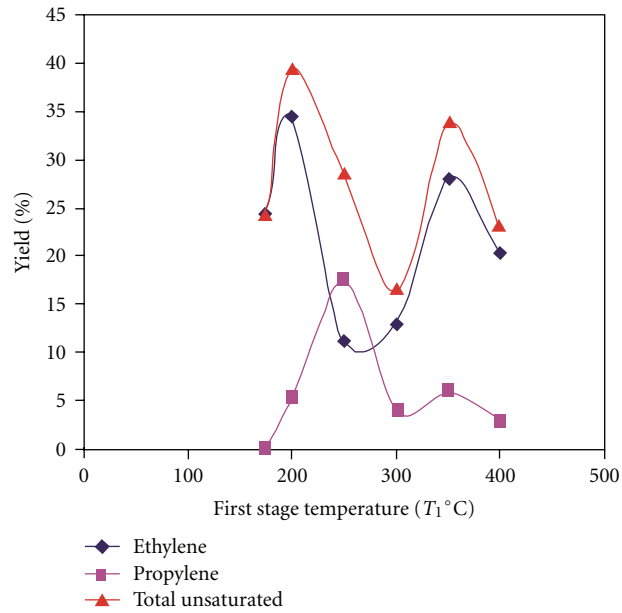

Figure 1: Influence of the first stage temperature (T_1) on the yield of unsaturated hydrocarbons.

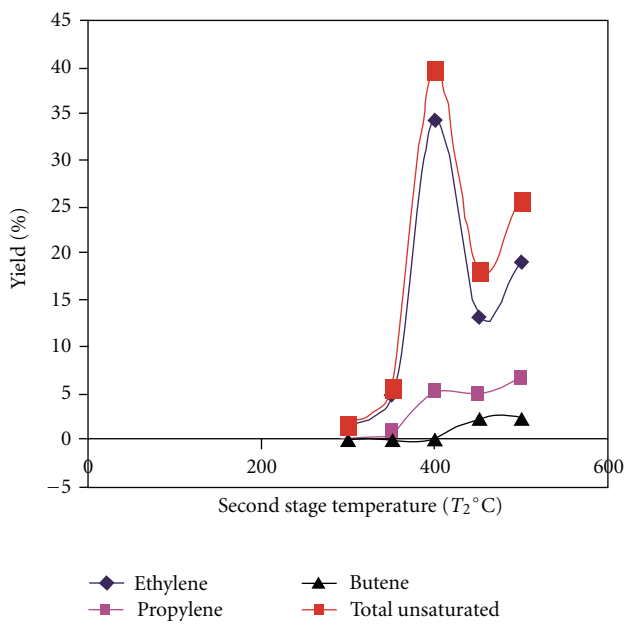

Figure 2: Influence of the second stage temperature (T_2) on the yield of unsaturated hydrocarbons.

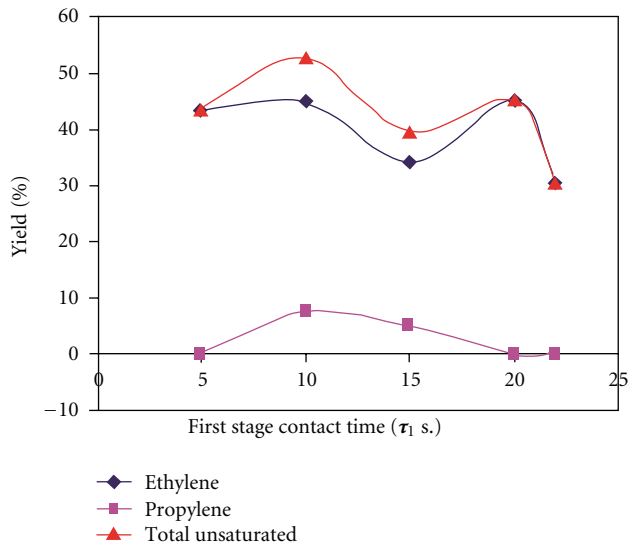

Figure 3: Influence of the first stage contact time (τ_1) on the yield of unsaturated hydrocarbons.

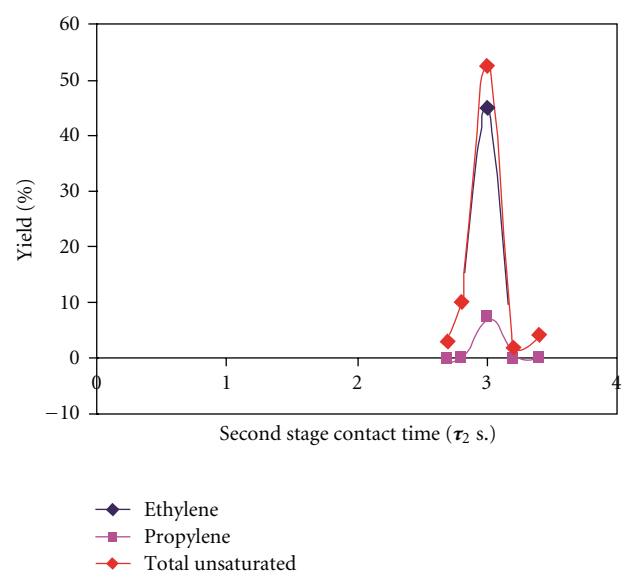

Figure 4: Influence of the second stage contact time (τ_2) on the yield of unsaturated hydrocarbons.

(10.53 wt. %). This confirms that the nanocatalyst with the rod shape is the optimum condition for ethylene production.

Studying the effect of using Pd-Au core-shell and alloy [17, 20–31], supported on the Cao catalyst on the distribution of the hydrocarbon pyrolyzate produced from two-stage catalytic pyrolysis of the feed stock fraction separated from Egyptian crude oil under the same last optimum conditions, with pear in mind that Palladium is used as a catalyst in hydrogenation reactions, when we use Pd-nanoparticles as a core in the catalytic pyrolysis, the total yield of unsaturated hydrocarbons will decrease and give yield (59.48 wt. %) total unsaturated hydrocarbons, mainly ethylene (51 wt. %), and propylene (8.48 wt. %), but the presence of palladium on the

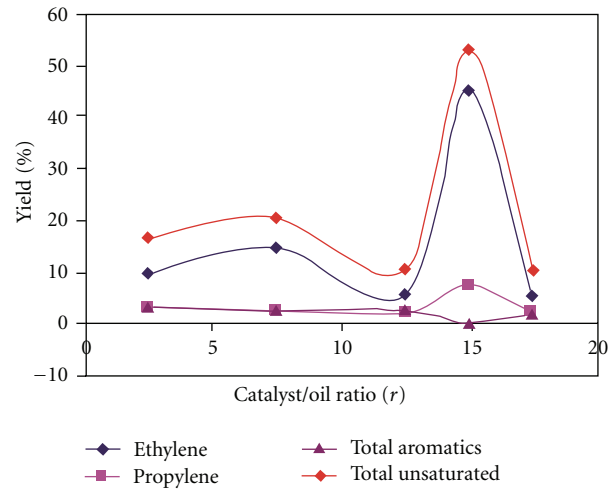

Figure 5: Influence of the catalyst/oil ratio on the yield of unsaturated hydrocarbons.

surface increases the rate of hydrogenation, contrary to down falling to the yield of the total unsaturated hydrocarbons to give 48.15 wt. %, mainly ethylene (40.2 wt. %), and propylene (7.95 wt. %), and increases the yield of ethane to reach 33.59 wt. % corresponding to 23.17 wt. % of ethane using Pd-Au core-shell.

7. Conclusion

It was found that the maximum yield of unsaturated hydrocarbons using the first catalyst (CaO) is about 54 wt. %, mainly hexene gives 29 wt. %, 12 wt. % ethylene, 12 wt. % aromatics, and ~1 wt. % propylene at the following conditions: $T_1 = 250^\circ$C, $T_2 = 400^\circ$C, $\tau_1 = 15$ min, $\tau_2 = 3$ sec and cat/oil ratio (r) 1 : 25, but by using the gold (Au) nanoparticles supported on the first catalyst, the maximum yield of unsaturated hydrocarbon is about 53 wt. %, mainly 45 wt. % ethylene and 8 wt. % propylene, only without aromatics at the following conditions: $T_1 = 200^\circ$C, $T_2 = 400^\circ$C, $\tau_1 = 10$ min, $\tau_2 = 3$ sec, and cat/oil (r) ratio 1 : 15, so Au-nanoparticles seem to be very selective to these reactions.

The Au nanocatalyst with rods shape gives the maximum yield of ethylene (which can be converted easily to ethyl alcohols which is used as E-85 clean fuel) from petroleum residues.

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