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## New Developed Equations for the Optimization of C<sub>2</sub>-C<sub>4</sub> Unsaturation through Three-Stage Pyrolysis

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### Keywords

Three-stage pyrolysis;  
Egyptian crude oil;  
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### Abstract

In three-stage flow-type silica reactor, pyrolysis of heavy fraction of Egyptian crude oil was carried out. Reaction variables were studied and the optimum conditions for the maximum yield of C<sub>2</sub>-C<sub>4</sub> individual and total unsaturates, were achieved. Through computational approach, each of the investigated parameters were plotted against the weight percentage of the produced individual unsaturates and a number of polynomial equations, were formulated. Application of platinum and palladium nanospheres with the catalysts was found to be suitable for increasing the yield of total unsaturates.

### Introduction

The large reserves of heavy oils in proportion to conventional crude oil, has sparked considerable interest in technologies for converting these feeds into products with more desirable characteristics. In the pyrolysis of atmospheric gas oil (AGO) and vacuum gas oil (VGO) under different cracking severities (B. Lohr., 1977; L.F. Hatch., 1978; S.B. Zdonik., 1967 and G.L. Hayward., 1975), the product distribution was also dependent on the composition of the feedstock and its specific properties.

In particular, the conversion of vacuum residue (boiling over 524°C) into distillates is of particular interest in improving the economic value despite the well-established technology for converting these residues by coking (P.S. Virk *et al.*, 1974 and S. Nowak *et al.*, 1975), hydroconversion, fluid catalytic cracking (FCC), and the three-stage pyrolysis technique of heavy oils proved to be an efficient process for the production of lower olefins (T. Suzuki *et al.*, 1982 and M. Itoh *et al.*, 1983). In this technique, residual was first

thermally cracked at high temperature to give pyrolyzed oil and pitch. The pyrolyzed oil was carried to the second and third high temperature stage and was further pyrolyzed to lower olefins. A similar process was developed by Kureha chemical industry Co. and Chiyoda Engineering and construction Co., as the Eureka process (T. Aiba., 1981). Platinum and Palladium supported on calcium oxides are widely used for naphtha reforming and for heavy linear paraffin dehydrogenation in the petrochemical industries (Miguel S.R *et al.*, 1995 and Pieck C.L. *et al.*, 2005). The dehydrogenation catalyst rapidly deactivates due to fouling by heavy carbonaceous materials. Silica is the most widely used support material for the dehydrogenation catalysts because of its superior capability to maintain a high degree of platinum dispersion which is essential for achieving high dehydrogenation activity. It has been reported that strong acidity of silica causes side reactions and coke formation (Bhasin M.M. *et al.*, 2001)

Driven by increasing gasoline prices, the market for gasoline alcohol blends is growing. With consumer demand for alternative fuel vehicles increasing, auto-manufacturers are working to produce flexible fuel vehicles, which are capable of operating ethanol-gasoline blends E10, E20, E85 (Ethanol 85 & gasoline 15) (Ethanol in America Handbook; 2012). Ethanol is a renewable, domestically produced fuel that can be made from grains, such as corn or wheat, or from biomass or cellulose sources, such as prairie grass and agricultural wastes.

Low molecular weight alcohol oxygenates are blended in gasoline to improve performance, combustion and emission characteristics of fuel-alcohol blends (X. Cu *et al.*, 2012; C. Jin *et al.*, 2011 and V. Surisetty *et al.*, 2011). More recently, the effects of dual alcohols with single alcohol blended in gasoline fuel have been studied to get better performance and emission (L. Siwale *et al.*, 2013, 2014). Other investigators have reported some results concerning the behavior of an ICE working with gasoline blended with a fraction rich in esters of carboxylic acids derived from biomass pyrolysis (Pelaz-Samanieg *et al.*, 2011).

Pyrolysis which are enriched in C<sub>2</sub>-C<sub>4</sub> unsaturated gases can be easily converted to the corresponding alcohols through the addition of water across the double bond. Catalytic hydrolysis gave good alcohol yield and excellent selectivity (Guangbin Dong *et al.*, 2011). Based on pyrolysis hydration assumptive process, alcohol oxygenates could be more easily produced than that obtained from grains, biomass, or agriculture wastes. This research paper addresses the optimization of C<sub>2</sub>-C<sub>4</sub> unsaturates from three-stage catalytic pyrolysis of a heavy residue of Egyptian crude oil in presence of platinum and palladium nanospheres over CaO or SiO<sub>2</sub> through computational approach, new developed equations were formulated. R<sup>2</sup> values shows the reliability of each fit.

## Experimental

### Materials

The physicochemical characteristic of the Egyptian crude oil used has been investigated once before (I.K. Basily *et al.*, 1993). The catalysts used; Ca<sup>++</sup>; have been supplied by "Union Carbide" Tarry Town technical center.

### Apparatus and procedure

The pyrolysis has been carried out using flow-type reactor fig(I), the pyrolyzate hydrocarbons were analyzed using gas chromatograph (A1/F1) under the following conditions; Column: 25mx 0.32mm fused silica WCOT CP-Sil 5 CP (1.2 micrometer), Detector: FID, Flow rate: 14.3 ml/min using He gas carrier, Inst. Type: Fractovap 2350.

## Result and Discussion

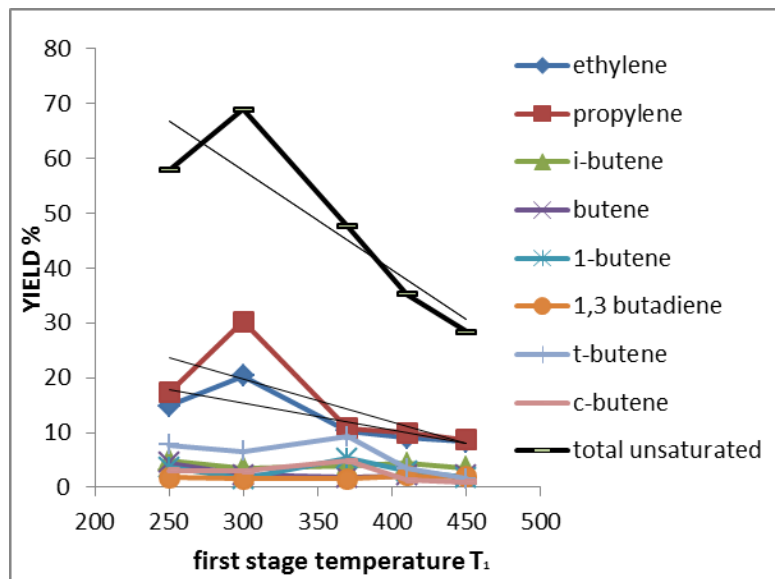
*The bearing of first stage temperature (T<sub>1</sub>) on the distribution of hydrocarbon pyrolyzates produced from catalytic Multi-stage pyrolysis of the tested feedstock fraction separated from the Egyptian crude oil using CaO catalyst :*

Preliminary experiments have been carried out to determine the optimum conditions for better performance for these reactions.

Fig (1), illustrate the influence of first-stage temperature (T<sub>1</sub>) on the distribution of the hydrocarbon pyrolyzate produced from catalytic Multi-stage pyrolysis of the feed stock fraction (A) separated from Egyptian crude oil using CaO catalyst, where all other factors (T<sub>2</sub>), (T<sub>3</sub>), (τ), oil/cat ratio of the second stage (R<sub>2</sub>), and oil/cat ratio of the third stage (R<sub>3</sub>) are kept constant at 350°C, 400 °C, 2.8 sec., 2, and 1.5, respectively.

The total unsaturated hydrocarbon pyrolyzates increased with increasing (T<sub>1</sub>) from 250 °C till 450 °C and reached ~ 69 wt. % at (T<sub>1</sub>) = 300 °C, and decreased by increasing (T<sub>1</sub>). As the first stage temperature increased from 250-300 °C, the yield of ethylene increased to reach 20.31 wt. % at 300 °C and decreased by increasing temperature, while % yield of propylene reached 30.1 wt. % at 300 °C and decreased by increasing temperature. It was found that when T<sub>1</sub>= 300 °C, T<sub>2</sub>= 350 °C, T<sub>3</sub>= 400 °C, τ = 2.8 sec., R<sub>2</sub>= 2, R<sub>3</sub>= 1.5, and severity (S) = 0.15, under these conditions we obtained the

maximum yield of unsaturated hydrocarbon pyrolyzates (69 wt. %).



**Fig.1** The influence of first-stage temperature ( $T_1$ ) in the distribution of the hydrocarbon pyrolyzate produced from catalytic Multi-stage pyrolysis of the feed stock fraction (A) separated from Egyptian crude oil using CaO

$$\text{Slope}_{(\text{ethylene})} = -0.05, \text{Slope}_{(\text{propylene})} = -0.08, \text{Slope}_{(\text{total unsaturated})} = -0.18$$

i.e. yield % total unsaturated is inversely proportional to ( $T_1$ )

Applying the developed polynomial equations for ethylene, propylene, and total unsaturated pyrolyzates as a function of ( $T_1$ ), was obtained as follow:

$$Y_{\text{ethylene}} = 1e^{-5}(T_1)^3 - 0.011(T_1)^2 + 4.04(T_1) - 435.4 \quad (R^2 = 1)$$

$$Y_{\text{propylene}} = 2e^{-5}(T_1)^3 - 0.024(T_1)^2 + 8.37(T_1) - 919.5 \quad (R^2 = 0.9123)$$

$$Y_{\text{total unsaturated}} = 2e^{-5}(T_1)^3 - 0.024(T_1)^2 + 8.75(T_1) - 911.4 \quad (R^2 = 0.9982)$$

*The influence of the third-stage temperature ( $T_3$ ) on the distribution of the hydrocarbon pyrolyzate produced from catalytic Multi-stage pyrolysis of the feed stock fraction (A) separated from Egyptian crude oil using CaO catalyst ( $Ca^{++}$ ):*

Fig (2), illustrate the influence of third-stage temperature ( $T_3$ ) on the distribution of the hydrocarbon pyrolyzate produced from catalytic Multi-stage pyrolysis of the feed stock fraction (A) separated from Egyptian crude oil using CaO catalyst, where all the factors ( $T_1$ ), ( $T_2$ ), ( $\tau$ ), oil/cat ratio of the second stage ( $R_2$ ), and oil/cat ratio of the third stage ( $R_3$ ) are kept constant at 300°C, 350 °C, 2.8 sec., 2, and 1.5, respectively.

The total unsaturated hydrocarbon pyrolyzates increased with increasing ( $T_3$ ) from

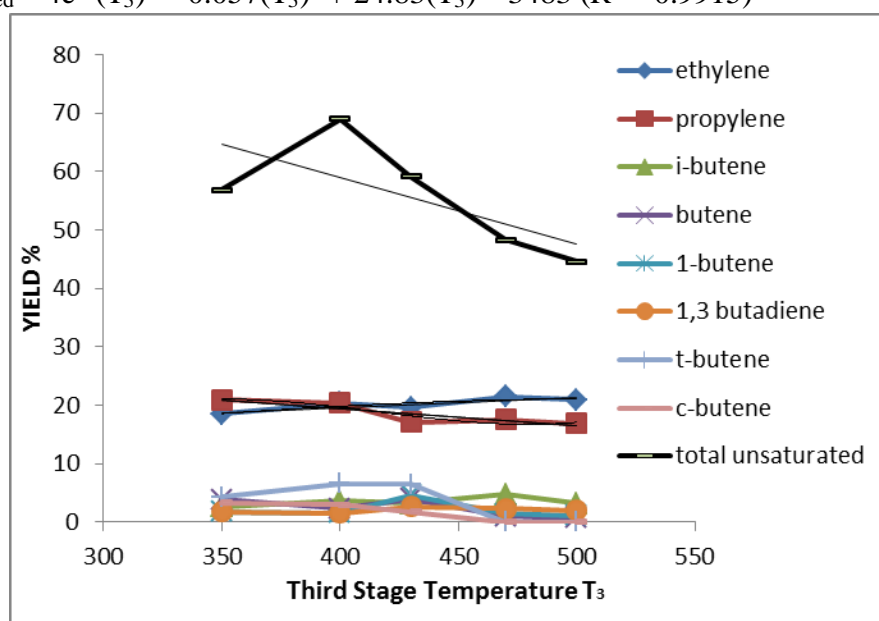
350°C up to 400°C and reached ~ 69 wt. % and decreased by increasing ( $T_3$ ). As the third stage temperature increased from 350-470°C, the yield of ethylene increased to reach 21.43 wt. % at 470°C and decreased by increasing temperature, while % yield of propylene reached 30.3 wt. % at 400 °C and decreased by increasing temperature. It was found that when  $T_1 = 300$  °C,  $T_2 = 350$  °C,  $T_3 = 400$  °C,  $\tau = 2.8$  sec.,  $R_2 = 2$ ,  $R_3 = 1.5$  & ( $S$ ) = 0.15, under these conditions we obtained the maximum yield of unsaturated hydrocarbon pyrolyzates (69 wt. %).

Applying the developed polynomial equations for ethylene, propylene, and total unsaturated pyrolyzates as a function of ( $T_3$ ), was obtained as follow:

$$Y_{\text{ethylene}} = -7e^{-8}(T_3)^3 + 7e^{-6}(T_3)^2 + 0.051(T_3) + 2.903 \quad (R^2 = 1)$$

$$Y_{\text{propylene}} = 4e^{-5}(T_3)^3 - 0.047(T_3)^2 + 20.12(T_3) - 2769 \quad (R^2 = 1)$$

$$Y_{\text{total unsaturated}} = 4e^{-5}(T_3)^3 - 0.057(T_3)^2 + 24.83(T_3) - 3483 \quad (R^2 = 0.9915)$$



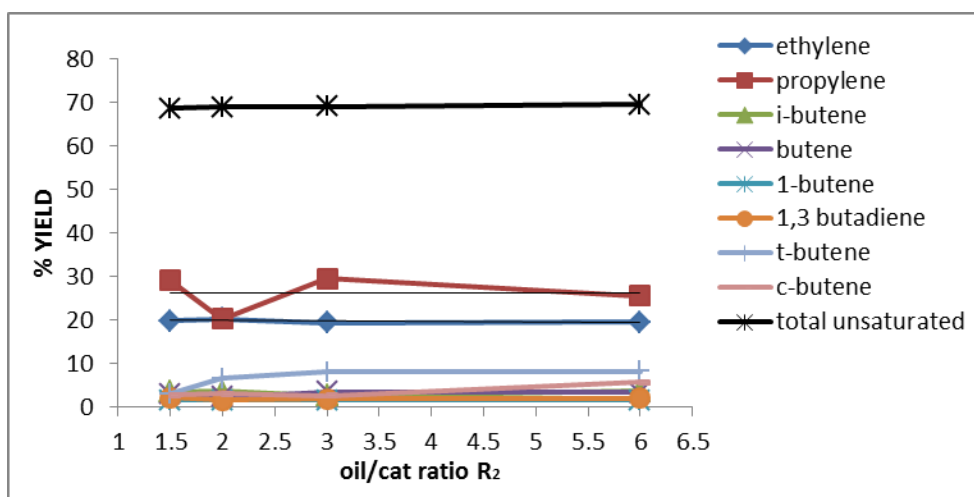
**Fig.2** The influence of third-stage temperature ( $T_3$ ) in the distribution of the hydrocarbon pyrolyzate produced from catalytic Multi-stage pyrolysis of the feed stock fraction (A) separated from Egyptian crude oil using CaO

$$\text{Slope}_{(\text{ethylene})} = 0.02, \text{Slope}_{(\text{propylene})} = -0.03, \text{Slope}_{(\text{total unsaturated})} = -0.11$$

*The influence of second-stage oil/cat ratio ( $R_2$ ) on the distribution of the hydrocarbon pyrolyzate produced from catalytic Multi-stage pyrolysis of the feed stock fraction (A) separated from Egyptian crude oil using CaO catalyst ( $\text{Ca}^{++}$ ):*

Fig (3), illustrate the influence of second-stage oil/cat ratio ( $R_2$ ) on the distribution of the hydrocarbon pyrolyzate produced from catalytic Multi-stage pyrolysis of the feed stock fraction (A) separated from Egyptian crude oil using CaO catalyst, where all other factors ( $T_1$ ), ( $T_2$ ), ( $T_3$ ), ( $\tau$ ), and oil/cat ratio of the third stage ( $R_3$ ) are kept constant at 300°C, 350 °C, 400°C, 2.8 sec., and 1.5, respectively.

The total unsaturated hydrocarbon pyrolyzates appeared unaffected by decrease the oil/cat ratio ( $R_2$ ) from 6 to 1.5 and hovering around 69 wt. %. As the ( $R_2$ ) increased, the % yield of ethylene revolves around ~20 wt. %, while % yield of propylene increased by decreasing ( $R_2$ ) and reached 30.3 wt. % at ( $R_2$ ) = 2 and became slightly constant by increasing ( $R_2$ ). It was found that when  $T_1 = 300^\circ\text{C}$ ,  $T_2 = 350^\circ\text{C}$ ,  $T_3 = 400^\circ\text{C}$ ,  $\tau = 2.8$  sec.,  $R_2 = 2$ ,  $R_3 = 1.5$ , & ( $S$ ) = 0.15, under these conditions we obtained the maximum yield of unsaturated hydrocarbon pyrolyzates (69 wt. %).



**Fig.4** The influence of oil/cat ratio ( $R_2$ ) in the distribution of the hydrocarbon pyrolyzate produced from catalytic Multi-stage pyrolysis of the feed stock fraction (A) separated from Egyptian crude oil using CaO

$$\text{Slope}_{(\text{ethylene})} = -0.1, \text{Slope}_{(\text{propylene})} = -0.004, \text{Slope}_{(\text{total unsaturated})} = 0.16$$

Applying the developed polynomial equations for ethylene, propylene, and total unsaturated pyrolyzates as a function of ( $r_2$ ), was obtained as follow:

$$Y_{\text{ethylene}} = -0.405(R_2)^3 + 2.95(R_2)^2 - 6.155(R_2) + 23.16 \quad (R^2 = 1)$$

$$Y_{\text{propylene}} = 0.17(R_2)^3 - 2.56(R_2)^2 + 10.37(R_2) + 17.64 \quad (R^2 = 1)$$

$$Y_{\text{total unsaturated}} = -0.115(R_2)^3 + 0.875(R_2)^2 - 2.2(R_2) + 70.97 \quad (R^2 = 1)$$

*The influence of third-stage oil/cat ratio ( $R_3$ ) on the distribution of the hydrocarbon pyrolyzate produced from catalytic Multi-stage pyrolysis of the feed stock fraction (A) separated from Egyptian crude oil using CaO catalyst ( $Ca^{++}$ ):*

Fig (4), illustrate the influence of third-stage oil/cat ratio ( $R_3$ ) on the distribution of the hydrocarbon pyrolyzate produced from catalytic Multi-stage pyrolysis of the feed stock fraction (A) separated from Egyptian crude oil using CaO catalyst, where all the factors ( $T_1$ ), ( $T_2$ ), ( $T_3$ ), ( $\tau$ ), and oil/cat ratio of the second stage ( $R_2$ ) are kept constant at 300°C, 350 °C, 400°C, 2.8 sec., and 2 respectively.

The total unsaturated hydrocarbon pyrolyzates increased by decreasing the oil/cat ratio ( $R_3$ ) till reached ~69 wt. % at  $R_3=1.2$  and decreased by decreasing  $R_3$ , also, the % yield of ethylene decreased by decreasing ( $R_3$ ), while

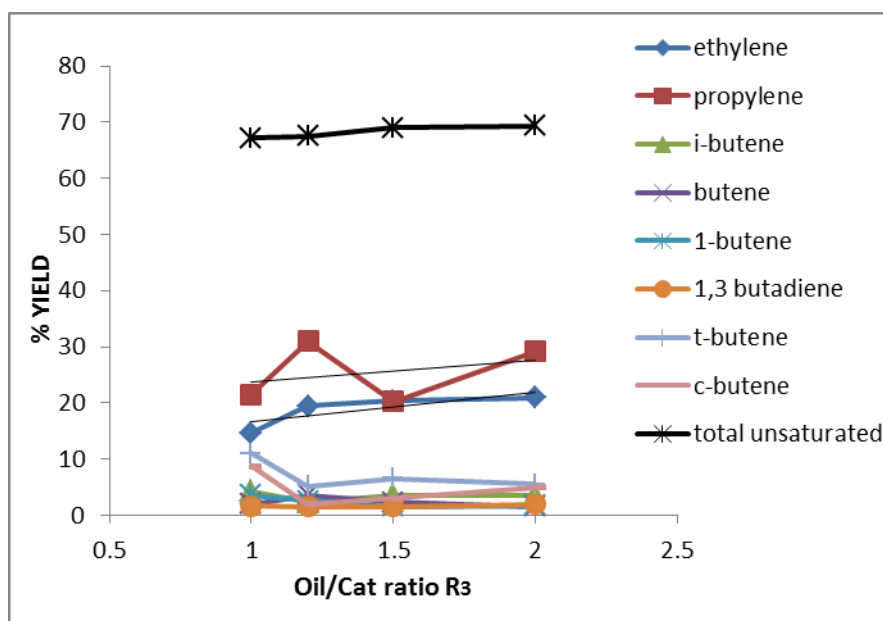
% yield of propylene increased by decreasing ( $R_3$ ) and reached 31 wt. % at ( $R_3$ ) = 1.2 and decreased by decreasing ( $R_3$ ). It was found that when  $T_1= 300^\circ\text{C}$ ,  $T_2= 350^\circ\text{C}$ ,  $T_3= 400^\circ\text{C}$ ,  $\tau = 2.8$  sec.,  $R_2= 2$ ,  $R_3= 1.5$ , and ( $S$ ) = 0.15, under these conditions we obtained the maximum yield of unsaturated hydrocarbon pyrolyzates (69 wt. %).

Applying the developed polynomial equations for ethylene, propylene, and total unsaturated pyrolyzates as a function of ( $R_3$ ), was obtained as follow:

$$Y_{\text{ethylene}} = 2.596(R_3)^3 - 33.7(R_3)^2 + 139.2(R_3) - 63.5 \quad (R^2 = 1)$$

$$Y_{\text{propylene}} = 4.68(R_3)^3 - 61.12(R_3)^2 + 255.7(R_3) - 314.2 \quad (R^2 = 1)$$

$$Y_{\text{total unsaturated}} = 0.586(R_3)^3 - 7.76(R_3)^2 + 32.29(R_3) + 26.52 \quad (R^2 = 1)$$



**Fig.4** The influence of oil/cat ratio (R3) in the distribution of the hydrocarbon pyrolyzate produced from catalytic Multi-stage pyrolysis of the feed stock fraction (A) separated from Egyptian crude oil using CaO

$$\text{Slope}_{(\text{ethylene})} = 5.25, \text{Slope}_{(\text{propylene})} = 3.9, \text{Slope}_{(\text{total unsaturated})} = 2.31$$

$$\text{Slope}_{(\text{severity})} = 0.1$$

*The influence of contact time ( $\tau$ ) on the distribution of the hydrocarbon pyrolyzate produced from catalytic Multi-stage pyrolysis of the feed stock fraction (A) separated from Egyptian crude oil using CaO catalyst ( $\text{Ca}^{++}$ ):*

Fig (5), illustrate the influence of contact time on the distribution of the hydrocarbon pyrolyzate produced from catalytic Multi-stage pyrolysis of the feed stock fraction (A) separated from Egyptian crude oil using CaO catalyst, where all the factors ( $T_1$ ), ( $T_2$ ), ( $T_3$ ), oil/cat ratio of the second stage ( $R_2$ ), and oil/cat ratio of the third stage ( $R_3$ ) are kept constant at 300°C, 350 °C, 400°C, 2, and 1.5 respectively.

The total unsaturated hydrocarbon pyrolyzates increased by increasing the contact time ( $\tau$ ) and reached ~ 69 wt. % at ( $\tau$ ) = 2.8 sec. and decreased by increasing ( $\tau$ ). The % yield of ethylene increased by increasing ( $\tau$ ) to reach 20.3 wt. % at 2.8 sec. and sharply decreased by

increasing ( $\tau$ ), while % yield of propylene increased by increasing ( $\tau$ ) and reached 30.3 wt. % at 2.8 sec. and sharply decreased by increasing ( $\tau$ ).

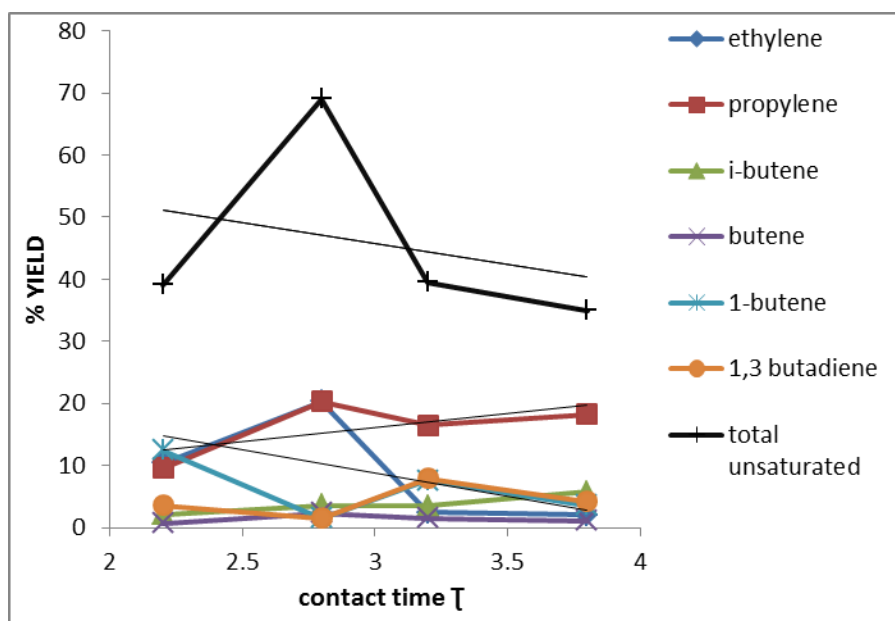
It was found that when  $T_1 = 300^\circ\text{C}$ ,  $T_2 = 350^\circ\text{C}$ ,  $T_3 = 400^\circ\text{C}$ ,  $\tau = 2.8$  sec.,  $R_2 = 2$ ,  $R_3 = 1.5$ , and ( $S$ ) = 0.15, under these conditions we obtained the maximum yield of unsaturated hydrocarbon pyrolyzates (69 wt. %).

Applying the developed polynomial equations for ethylene, propylene, and total unsaturated pyrolyzates as a function of ( $\tau$ ), was obtained as follow:

$$Y_{\text{ethylene}} = 65.57(\tau)^3 - 598.7(\tau)^2 + 1774(\tau) - 1694 \quad (R^2 = 1)$$

$$Y_{\text{propylene}} = 66.47(\tau)^3 - 614(\tau)^2 + 1852(\tau) - 1805 \quad (R^2 = 1)$$

$$Y_{\text{total unsaturated}} = 118.5(\tau)^3 - 1095(\tau)^2 + 3293(\tau) - 3167 \quad (R^2 = 1)$$



**Fig.5** The influence of contact time ( $\tau$ ) on the distribution of the hydrocarbon pyrolyzate produced from catalytic Multi-stage pyrolysis of the feed stock fraction (A) separated from Egyptian crude oil using CaO

Slope<sub>(ethylene)</sub> = -7.57, Slope<sub>(propylene)</sub> = 4.56, Slope<sub>(total unsaturated)</sub> = -6.73  
 i.e. yield % of propylene is directly proportional to contact time ( $\tau$ )

*The influence of flow rate of feedstock (F) on the distribution of the hydrocarbon pyrolyzate produced from catalytic Multi-stage pyrolysis of the feed stock fraction (A) separated from Egyptian crude oil using CaO catalyst ( $Ca^{++}$ ):*

Fig (6), illustrate the influence of flow rate of feedstock (F) on the distribution of the hydrocarbon pyrolyzate produced from catalytic Multi-stage pyrolysis of the feed stock fraction (A) separated from Egyptian crude oil using CaO catalyst, where all the factors ( $T_1$ ), ( $T_2$ ), ( $T_3$ ), oil/cat ratio of the second stage ( $R_2$ ), oil/cat ratio of the third stage ( $R_3$ ), and contact time are kept constant at 300°C, 350 °C, 400°C, 2, 1.5, and 2.8 sec., respectively.

The total unsaturated hydrocarbon pyrolyzates increased by increasing the oil flow rate (F) from 25-30 ml/hr. and reached ~ 69 wt. % at (F) = 30ml/hr. and decreased by increasing (F). The % yield of ethylene

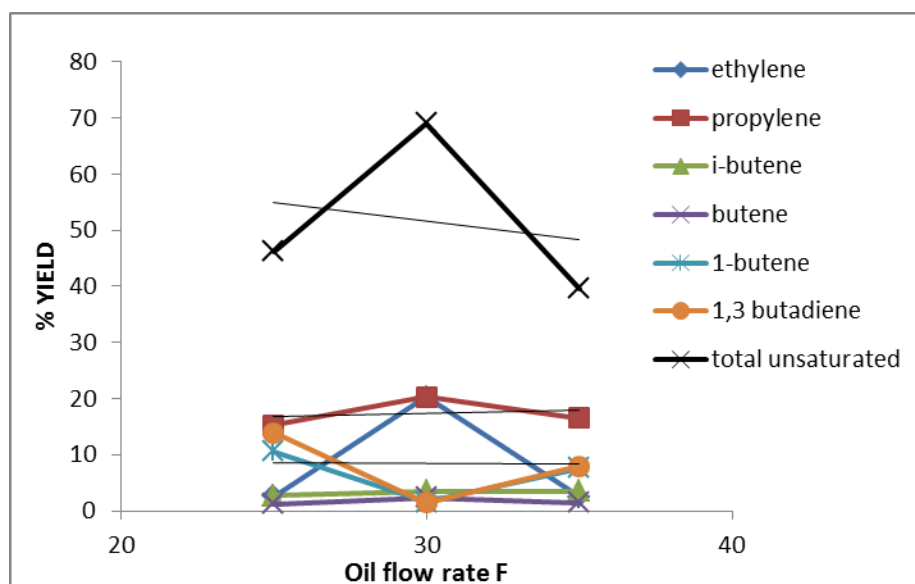
increased by increasing (F) to reach 20.31 wt. % at 30 ml/hr. and decreased by increasing (F), however, % yield of propylene increased by increasing (F) and reached 30.3 wt. % at 30 ml/hr. and sharply decreased by increasing (F). It was found that when  $T_1 = 300^\circ C$ ,  $T_2 = 350^\circ C$ ,  $T_3 = 400^\circ C$ ,  $\tau = 2.8$  sec.,  $R_2 = 3.1$ ,  $R_3 = 2.4$ , and (F) = 30 ml/hr.; severity (S) = 0.15; under these conditions we obtained the maximum yield of unsaturated hydrocarbon pyrolyzates (69 wt. %).

Applying the developed polynomial equations for ethylene, propylene, and total unsaturated pyrolyzates as a function of (F), was obtained as follow:

$$Y_{\text{ethylene}} = -0.711(F)^2 + 42.64(F) - 619.2 \quad (R^2 = 1)$$

$$Y_{\text{propylene}} = 0.577(F)^2 + 34.74(F) - 492.8 \quad (R^2 = 1)$$

$$Y_{\text{total unsaturated}} = -1.044(F)^2 + 61.98(F) - 850.6 \quad (R^2 = 1)$$



**Fig.6** The influence of oil flow rate (F) on the distribution of the hydrocarbon pyrolyzate produced from catalytic Multi-stage pyrolysis of the feed stock fraction (A) separated from Egyptian crude oil using CaO

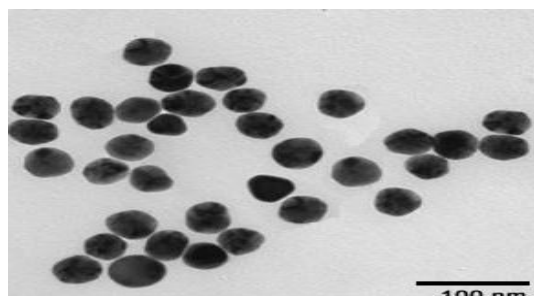
$$\text{Slope}_{(\text{ethylene})} = -0.01, \text{Slope}_{(\text{propylene})} = 0.13, \text{Slope}_{(\text{total unsaturated})} = -0.67$$

$$\text{Slope}_{(\text{severity})} = 0.1$$

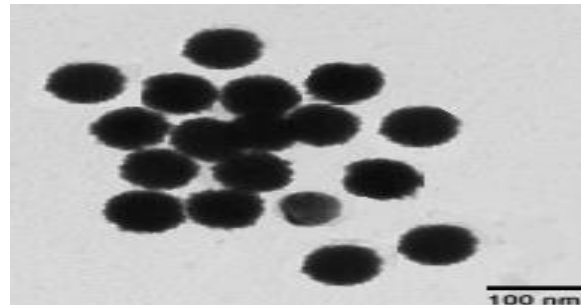
*Study the effect of Platinum (Pt) and Palladium (Pd) Nano-particles (supported on different types of supports) on the yield of unsaturated hydrocarbon pyrolyzates produced from multi-stage catalytic cracking of feedstock (A) separated from Egyptian crude oil:*

Under the same optimum conditions at which the maximum yield of unsaturated hydrocarbons produced from multi-stage catalytic cracking of the feedstock fraction (A) using CaO ( $\text{Ca}^{++}$ );  $T_1=300^\circ\text{C}$ ,  $T_2=350^\circ\text{C}$ ,  $T_3=400^\circ\text{C}$ ,  $R_2=2$ ,  $R_2=1.5$ ,  $\tau = 2.8$  sec., and

severity (S) = 0.15, a comparison between the yield of the total unsaturated hydrocarbon pyrolyzates using CaO, Pt supported on CaO (Pt/CaO), Pt supported on silica (Pt/SiO<sub>2</sub>), Pd supported on CaO (Pd/CaO), and Pd supported on silica (Pd/SiO<sub>2</sub>) takes place, as shown in table (1), fig (a) & (b) shows TEM for platinum and palladium nanosphere. From the table, it revealed the maximum unsaturated hydrocarbons is obtained by using Pd/CaO was 91.65 wt. % mainly ETHYLENE 88.21 wt. % and traces of propylene compared with ethylene.



(a) TEM for Pt nanospheres



(b) TEM For Pd nanospheres



**Table 1:** Study the effect of Platinum (Pt) and Palladium (Pd) Nano-particles (supported on different supports) on the yield of unsaturated hydrocarbon pyrolyzates produced from multi-stage catalytic cracking of feedstock (A) separated from Egyptian crude oil

Run no.	1	2	3	4	5
1st stage temperature	300	300	300	300	300
2nd stage temperature	350	350	350	350	350
3rd stage temperature	400	400	400	400	400
contact time (T)	2.8	2.8	2.8	2.8	2.8
2nd stage oil/cat ratio (r2)	3.1	3.1	3.1	3.1	3.1
3rd stage oil/cat ratio (r3)	2.4	2.4	2.4	2.4	2.4
Oil flow rate (F)	30	30	30	30	30
severity (S)	0.15	0.15	0.15	0.15	0.15
<b>Type of catalyst:</b>	<b>CaO</b>	<b>Pt/SiO<sub>2</sub></b>	<b>Pt/CaO</b>	<b>Pd/SiO<sub>2</sub></b>	<b>Pd/CaO</b>
methane	17.87	4.31	4.68	3.21	3.3
<b>ethylene</b>	<b>20.31</b>	<b>51.11</b>	<b>55.28</b>	<b>77.02</b>	<b>88.21</b>
ethane	3.78	3.2	4.62	4.62	2.63
<b>propylene</b>	<b>20.3</b>	<b>13.91</b>	<b>25.65</b>	<b>11.01</b>	<b>3.44</b>
propane	4.51	4.52	2.79	4.13	2.43
iso-butane	1.43	2.6	2.51	0	0
<b>iso-butene</b>	<b>3.56</b>	<b>6.7</b>	<b>2.51</b>	<b>0</b>	<b>0</b>
<b>1-butene</b>	<b>2.31</b>	<b>13.85</b>	<b>4.34</b>	<b>0</b>	<b>0</b>
<b>1,3 butadiene</b>	<b>1.52</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>
<b>n-butane</b>	<b>1.51</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>
<b>t-butene</b>	<b>6.54</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>
<b>c-butene</b>	<b>3.41</b>	<b>0</b>	<b>0</b>	<b>0</b>	<b>0</b>
iso-pentane	2.97	0	0	0	0
<b>Total unsaturated</b>	<b>69.02</b>	<b>85.57</b>	<b>87.78</b>	<b>88.03</b>	<b>91.65</b>
ΣC <sub>2</sub> unsat.+C <sub>2</sub> sat./	0.63	3	2	5.7	13.4
ΣC <sub>1</sub> + C <sub>3</sub> unsat..					

Pt/SiO<sub>2</sub>, Pt/CaO, Pd/SiO<sub>2</sub> gave also satisfactory results for the % yield of unsaturated hydrocarbon; 85.57 wt. % (ethylene 51.11 wt. %, propylene 13.91 wt. %, butene 20.55 wt. %), 87.78 wt. % (ethylene 55.28 wt. %, propylene 25.65 wt. %, butene 6.85 wt. %), and 88.03 wt. % (ethylene 77 wt. %, propylene 11.01 wt. %) respectively. Accordingly, Pd/CaO gives the ideal choice for specialty and production of ETHYLENE for feedstock (A).

## Conclusion

The Multi-stage pyrolysis technique not only decreases the temperature, but also increases the unsaturated hydrocarbon pyrolyzates by optimization of instrumental pyrolysis parameter.

Using CaO catalyst, we can control the yield of unsaturated pyrolyzates as follows:

$$Y_{\text{ethylene}} = 0.2e^{-5}(T_1)^3 - 0.002(T_1)^2 + 0.808(T_1) - 1.4e^{-8}(T_3)^3 + 1.4e^{-6}(T_3)^2 + 0.01(T_3) - 0.081(R_2)^3 + 0.59(R_2)^2 - 1.231(R_2) + 0.5192(R_3)^3 - 6.74(R_3)^2 + 27.84(R_3) + 13.114(\tau)^3 - 119.74(\tau)^2 + 354.8(\tau) - 0.142(F)^2 + 8.52(F) - 557.21$$

$$Y_{\text{propylene}} = 0.4e^{-5}(T_1)^3 - 0.004(T_1)^2 + 1.674(T_1) + 0.8e^{-5}(T_3)^3 - 0.01(T_3)^2 + 4.024(T_3) + 0.034(R_2)^3 - 0.512(R_2)^2 + 2.074(R_2) + 0.94(R_3)^3 - 12.22(R_3)^2 + 51.14(R_3) + 13.294(\tau)^3 - 122.8(\tau)^2 + 370.4(\tau) + 0.1154(F)^2 + 6.948(F) - 1256.57$$

$$Y_{\text{total.unsaturated}} = 0.4e^{-5}(T_1)^3 - 0.004(T_1)^2 + 1.75(T_1) + 0.8e^{-5}(T_3)^3 - 0.011(T_3)^2 + 4.966(T_3) - 0.023(R_2)^3 + 0.175(R_2)^2 - 0.44(R_2) + 0.1172(R_3)^3 - 1.552(R_3)^2 + 6.458(R_3) + 23.7(\tau)^3 - 219(\tau)^2 + 647.8(\tau) - 0.208(F)^2 + 12.396(F) - 1662.9$$

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## معادلات متقدمة جديدة لتعظيم الاستفادة من الهيدروكربونات الغير مشبعة من خلال ج التكسير ثلاثي المرحلة

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اثبتت عملية التكسير الحفزي ثلاثي المرحلة نجاحا كبيرا في هذا المجال في الآونة الاخيرة ففي المرحلة الاولى من التكسير تتحول المخلفات الثقيلة الي غازات بفعل الحرارة ثم يتم نقل هذه الغازات الناتجة الي المرحلة الثانية ثم المرحلة الثالثة بواسطة غاز الارجون لمزيد من التكسير الحفزي دون ادني تأثير لهذه الملوثات علي الحفاز المستخدم (حيث ان النسبة العظمي من هذه الملوثات تتجمع في المرحلة الاولى سينعدم تأثيرها في المرحلة الثانية والثالثة).

ولقد ساعدت هذه الطريقة علي استخدام العديد من العوامل الحفازة والتي يصعب استخدامها في طرق التكسير العادية ، كما اطالت هذه الطريقة الفترات الزمنية بين اعادة تنشيط الحفاز مما ادي الي اطالة عمر الحفاز ذاته وبذلك يتم الاستفادة من المخلفات البترولية العديدة والتي تمثل نسبة عالية من مكونات البترول .

تم في هذه الرسالة الاتي:

- (١) دراسة تأثير كل من درجات الحرارة في المرحتين الاولى ( $T_1$ ) و الثالثة ( $T_3$ ) و زمن التلامس في المرحلة الاولى و الثالثة و نسبة الحفاز الي الزيت علي توزيع نواتج التكسير الحفزي ثلاثي المرحلة باستخدام حفاز اكسيد الكالسيوم لمخلفات الزيت الغازي المستخلص من البترول المصري.
- (٢) دراسة استخدام البلاديوم في حجم النانو محمل علي  $CaO$  و  $SiO_2$  و ايضا البلاتين في حجم النانو محمل علي  $CaO$  و  $SiO_2$  و تأثيرهم علي توزيع نواتج التكسير ثلاثي المرحلة .