



## HYDRO-DE-AROMATIZATION OF PARAFFIN WAX

Dr. Ammar S. Abbas

Suondos K. A. Barno

Chemical Engineering Department,

College of Engineering - University of Baghdad

### ABSTRACT

Iraqi paraffin wax (1.0 wt% aromatic content and 4.4 wt% oil content, Basrah origin) was hydrotreated over commercial Pt-Re/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst in order to study aromatic removal reaction (de-aromatization) kinetics. Reaction temperature varied from 453 to 533 K over a liquid hourly space velocity from 0.5 to 4.2 h<sup>-1</sup>. Hydrogen pressure was kept constant throughout all the experiment at 3.6 Mpa with hydrogen to wax ratio about 400 m<sup>3</sup>/m<sup>3</sup>.

Kinetics analysis showed that the hydro-de-aromatization reaction followed a second order kinetics model. Energy, enthalpy and entropy of activation of hydro-de-aromatization reaction were 17.2 kJ/mole, 13.1 kJ/mole and -16.9 J/mole K, respectively.

### الخلاصة

تم هدرجة شمع برفافيني عراقي المنشأ (نتائج من عملية تكرير نفط البصرة) ذو محتوى زيتي 4.4 % وزناً و 1.0 % وزناً مواد اروماتية بأستعمال عامل مساعد Pt-Re/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> وذلك لدراسة حركية تفاعل ازالة المواد الاروماتية. تراوحت درجة حرارة التفاعل بين 453 و 533 كلفن و سرعة سائل فراغية بين 0.5 و 4.2 ساعة<sup>-1</sup>. ثبت ضغط الهيدروجين المستعمل و لكل التجارب بمقدار 3.6 ميكا باسكال و نسبة هيدروجين الى شمع 400 م<sup>3</sup>/م<sup>3</sup>.

اشارت النتائج الى ان موديل حركية التفاعل هي من الدرجة الثانية و كانت مقدار طاقة التنشيط للتفاعل 17.2 كيلو جول /مول و انتالبيية التنشيط 13.1 كيلو جول /مول و انتروبية التنشيط - 16.9 جول /مول كلفن.

### KEYWORDS

Hydro-de-aromatization, kinetics model, paraffin wax, activation energy.

### INTRODUCTION

Wax usually refers to a substance that is a plastic solid at ambient temperature and, no being subjected to moderately elevated temperatures, becomes a low viscosity liquid. The chemical composition of waxes is complex. They usually contain a broad variety of molecular weight species and reactive functional groups, although some classes of mineral and synthetic waxes are totally hydrocarbon compounds (Kirk-Othmer, 1984).

Waxes can be obtained from different sources: Natural (animals, insects, plants and lignite), petroleum and synthetics. As sources, the methods of wax separation differ from a simple mechanical impression (like in production of carnauba wax from leaves) to complex operations as like as de-waxing and de-oiling. The present petroleum wax industry resulted from demand for

better lubricants. Originally wax was a by-product in the de-waxing of lubricants oils and gas oils; soon, however, many industrial applications were found (Hobson, 1982).

The chemical compositions of natural waxes are usually containing different amounts of fatty alcohol, acids and esters. While, the chemical compositions of petroleum waxes are containing mainly paraffin and small amounts of iso-paraffin, cycloalkanes and aromatics (monocyclic and polycyclic aromatics). Generally, aromatics are cause a color change. This low color stability of waxes containing high aromatics is due to oxidation of aromatics (Liener, 1969), Purity criteria, including whiteness and color stability, calls for refinement of paraffin products (Ferund et al, 1982).

In order to reach this purity of waxes, many purification operations are used essentially for petroleum waxes. After de-waxing and de-oiling of petroleum waxes, additional purification processes can be used such as: treatment with chemicals (such as treatment with fuming sulfuric acid), treatment with clays (adsorption or bleaching process) and/or hydrogenation (Ferund et al, 1982 and Kalichevsky, 1956).

Hydrotreating processes (HD) can essentially be classified into two groups: Those significantly changing the physical and chemical properties of the feedstock, and those whose objective is final purification of the products, with partly changing the chemical and physical properties.

The feedstocks for the process belong the first groups are not so much the crude paraffin, but rather lubricating oil fractions and distillation residues. In both cases macro- and microcrystalline waxes are obtained from distillation and de-waxing of the hydrogenated petroleum products. The paraffin waxes are then subjected to some post-treatment, e.g. claying

The processes belonging to the second groups are widely used for various purposes. These are the feedstock preparation for catalytic, desulfurization of diesel fuels, pretreatment of heavy oil feedstock prior to catalytic cracking, improving combustion properties and color stability of kerosene, lubricating oils and waxes (Speight, 1981).

Many commercial hydrotreating processes for purification of paraffin liquids and wax are now available, but essentially they do not differ much. Their operating conditions are usually 250 – 300° C temperature, 0.6 – 9 Mpa hydrogen pressure, 0.5 – 10 h<sup>-1</sup> LHSV and recycle ratio 200 – 5000 m<sup>3</sup>/m<sup>3</sup> (Ferund et al, 1982).

Hydrogenation experiments were carried out by Lipvskaya and Agafonov (Lipvskaya and Agafonov, 1976) on de-oiled paraffin waxes obtained from vacuum distillation of sulfur-containing west-Siberian paraffin crude. The hydrogenation of the paraffin waxes containing 0.3 wt% oil, in the present of aluminum-platinum catalysts carried out using 250-300° C, 4000 kpa, liquid hourly space velocity (LHSV) of 0.5-1.0 h<sup>-1</sup> and hydrogen recycling ratio of 600 m<sup>3</sup>/m<sup>3</sup>. The produce wax melting point for wax obtained by de-waxing of 360-400° C boiling-range fraction is 54° C, while melting point of wax obtained by de-waxing of 400-490° C boiling-range fraction is 58° C. Both products were fully satisfactory for food industry requirement regarding to color, color stability and carcinogen content.

For medicinal white oil produce, solvent de-waxed raffinate with density of about 867 kg/m<sup>3</sup> at 15° C was hydrogenated over a mixed bed composed of 4.29 g of a commercial 0.6 wt % Pt on alumina reforming catalyst and 5.84 g of zinc oxide (ZnO). The used operating conditions are reaction temperature of 200 - 250° C, LHSV over the total catalyst charge of 1 to 4h<sup>-1</sup> and pressure of 6.9 Mpa (1000 psig). Aromatic reduction is extremely high (80 %) at 200° C and LHSV of 1h<sup>-1</sup>. Three hydrotreating stages of solvent de-waxed raffinate in series are recommended to produce high quality medicinal and food grade white oil (Hantzer et al, 2001).

The aim of this work is argument the hydro-de-aromatization reaction of paraffin wax; study the kinetics model of this reaction and evaluated activation energy, enthalpy and entropy of the hydro-de-aromatization reaction.



## EXPERIMENTAL WORK

### Raw Materials

- Paraffin wax: Iraqi paraffin wax (Basrah origin), the chemical and physical properties are shown in **Table (1)**.

Table (1). Chemical and physical properties of Iraqi paraffin wax.

Property		Test Methods
Melting point, ° C	66	ASTM D-127
Congeaing point, ° C	63	ASTM D-938
Oil content, wt%	4.4	ASTM D-721
Penetration, mm	21	ASTM D-5
Color	2.0	ASTM D-1500
Ash, wt%	0.17	ASTM D-482
Aromatics (UV), wt%	1.00	Discribed in experimental work
Aromatics (LSC), wt%	0.96	

- Catalyst: Platinum and rhenium supported over high purity alumina (CRITERION PR-29) was used as a hydrotreatment catalyst. Catalyst properties are given in **Table (2)**.

Table (2). Properties of commercial catalyst Pt-Re/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>.

Properties	Value	Properties	Value
Platinum, wt%	0.22	Normal size, mm	2.1
Rhenium, wt%	0.42	Compacted bulk density, kg/m <sup>3</sup>	710
Chloride, wt%	1.05	Surface area, m <sup>2</sup> /g	210
Al <sub>2</sub> O <sub>3</sub> , wt%	Balance	Pore volume, cm <sup>3</sup> /g	0.54
Shape	Cylinder	Anvil crush strength, N/cm	200

### Hydrotreating Experiments

The hydrotreating runs were preformed in a pilot plant continuous high-pressure unit employing an up-flow co-current.

The reactor is stainless steel, and heat resisting steel with dimensions of 650 mm length 20 mm in diameter. The reactor was jacketed with 4 separately heat controlled block shells in order to ascertain isothermal operation.

The reactor products were cooled in a condenser-cooler and separated from hydrogen un-reacted and the hydrocarbon gases by passing into high and low-pressure separators. The gases were then vented to the exterior through a gas flow meter. The unit was supplied with a high pressure-dosing pump to introduce the feedstock into the unit.

The reaction conditions employed are temperatures of 453 to 533 K, pressure of 3.6 Mpa, LHSV of 0.5 to 4.2h<sup>-1</sup> and hydrocarbon oil ratio of 400 m<sup>3</sup>/m<sup>3</sup>. Products were collected only after steady-state operation was established and initial operating products were discarded. The reactor was packed with about 60 cm<sup>3</sup> of the commercial Pt-Re-alumina type catalyst (after drying at 393 K for 2 h) between two layers of inert material (glass beads with 4 mm diameter).

### Determination of Aromatic Content

Siryuk and co-workers (Siryuk et al, 1975) found a useful method to determined aromatic content of heavy oils and waxes by using ultra-violet spectrometry techniques (UV).

This technique was developed by Abbas (Abbas, 2002) for Iraqi paraffin wax and the content of benzene, naphthalene and phenanthrene hydrocarbons ( $C_b$ ,  $C_n$  and  $C_p$ ) are determined in according with the formulas:

$$C_b(\text{wt}\%) = 0.859k_{200} - 0.164k_{230} - 0.254k_{255} \quad (1)$$

$$C_n(\text{wt}\%) = 0.027k_{200} + 0.553k_{220} - 0.142k_{255} \quad (2)$$

$$C_p(\text{wt}\%) = 0.002k_{200} - 0.019k_{230} + 0.801k_{255} \quad (3)$$

The above set of equations (Eq. 1 to 3) use only when  $k_{255} / k_{269}$  is less than 1 and  $k_{300}$  is greater than 0.001. If not, total aromatics content CA is calculated as:

$$C_A(\text{wt}\%) = \frac{k_{269}}{2.4} \quad (4)$$

$k$  is the specific extinction coefficient at wave length 200, 230, 255, 269 and 300 nm.

$$k = \frac{D}{CW * d} \quad (5)$$

Where  $D$  = absorbency,  $CW$  = g of wax / liter of iso-octane, and  $d$  = thickness of layer in cm. Shimadizu UV-160 was used to determine the absorbency by using 1 cm cell width (1 cm layer thickness).

The common method for aromatics content determination is obtained by liquid-solid chromatography (LSC) using silica-gel as the adsorbent.

Column of 10-mm diameter were packed to a high of 500 mm with silica-gel (mesh 35-70) which had been freshly generated at 383 K (110°C) overnight. 1g of sample was introduced into column and the saturated fraction was eluted from the column with 150 cm<sup>3</sup> of n-hexane, then aromatic fraction was eluted with 200 cm<sup>3</sup> of benzene. Finally, the polar aromatic fraction was eluted with 150 cm<sup>3</sup> of methanol-benzene mixture (20:80 by volume). Each fraction was recovered by evaporating of solvents.

UV method was used to determine aromatic content in feedstock and all product samples, while LSC method was used only for feedstock and final selected product. Comparison the results show little difference of aromatics content in waxes determined by using UV method and LSC.

## RESULTS AND DISCUSSION

### Effect of LHSV and Temperature on the Aromatic Removal

The removal of aromatic hydrocarbons due to hydrotreating process is increasing with temperature and with decreasing LHSV as shown in Fig. (1). These results are in good agreement with the studies of hydrotreating of heavy residues and waxes which are reported that the impurities removal increasing with temperature and decreasing with LHSV (Abbas, 1999, Hummadi, 1999, Mohammed and Abbas, 2001 and Hantzer et al, 2001).

The increasing aromatic removal at higher reaction temperature may be attributed to several reasons. First, the large aromatic molecules are decomposed onto smaller molecules, which came more easily diffuse into the catalyst micropores and reach the inner active sites where the de-aromatization reaction occurs. Second, the increasing of feedstock diffusivity due to decreases in the viscosity as a result of temperature increasing.

As LHSV decreases, hydro-de-aromatization reaction (aromatic removal) increasing due to the increasing in contact time between the feedstock and hydrogen over the active sites of catalyst.

Also, it can be noticed that at low LHSV ( $\leq 1$ ), temperature has no highly significant on aromatic removal.

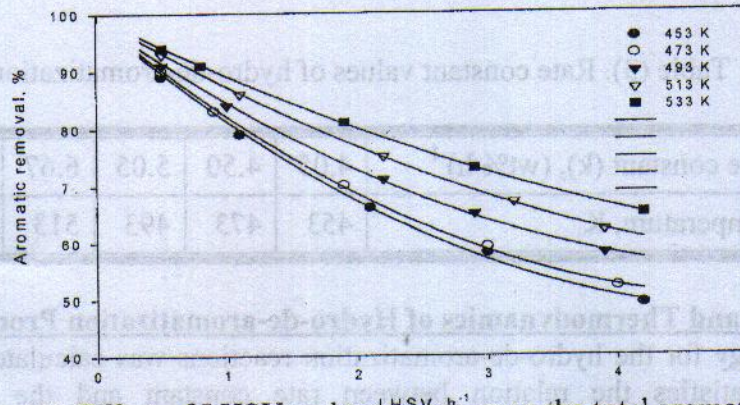


Fig. (1). Effect of LHSV and temperature on the total aromatic removal.

Aromatic removal from Iraqi paraffin wax is between 50 up to 93 % in the range of 0.5 - 4.2 h<sup>-1</sup> LHSV and temperature of 453 – 533 K. About 80 - 82 % of aromatic hydrocarbons are removed at 473 K temperature, 3.6 Mpa pressure and 1 h<sup>-1</sup> LHSV, this result is in good agreement with the results of aromatic removal of medicinal white oil, which is about 80 % at the same conditions but pressure is 6.9 Mpa (Hantzer et al, 2001).

**Kinetics Model of Hydro-de-aromatization (Aromatic Removal)**

Kinetics studies for data obtained from laboratory unit or pilot-plant scale usually play an important role in modeling and scale-up designs for new units.

Data obtained from the pilot-plant unit for the hydro-de-aromatization of Iraqi paraffin wax were analyzed by available kinetics models (Levenspiel, 1972). The governing equation for the hydrotreating reactor performance when the hydro-de-aromatization reaction supposed to be first-order may be expressed as:

$$\ln\left(\frac{C_{AF}}{C_A}\right) = \frac{k}{LHSV} \tag{6}$$

And: when the reaction supposed to be second-order, as:

$$\frac{1}{C_A} - \frac{1}{C_{AF}} = \frac{k}{LHSV} \tag{7}$$

Aromatic removal appeared to obey the ideal second-order kinetics equation with negligible deviation from plug flow, as shown in Fig. (2). The rate constants at each temperature can be easily evaluated from the straight lines slope.

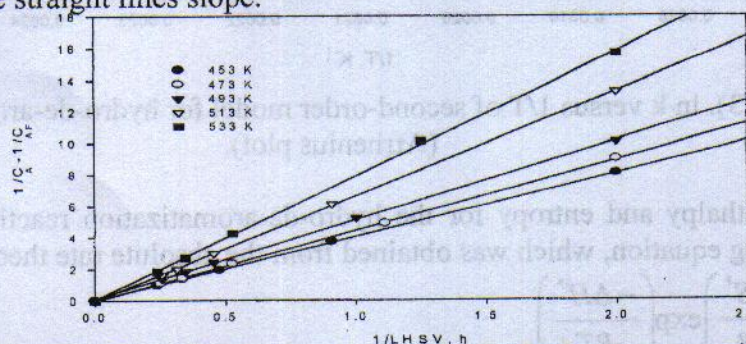


Fig. (2). Second-order kinetics model for hydro-de-aromatization.

The values of the rate constants for hydro-de-aromatization appears to increase with temperature and the rate constants are ranging between  $4.05 \text{ (wt\% \cdot h)}^{-1}$  at 453 K to  $7.88 \text{ (wt\% \cdot h)}^{-1}$  at 533 K, as shown in **Table (3)**.

Table (3). Rate constant values of hydro-de-aromatization.

Rate constant (k), $(\text{wt\% h})^{-1}$	4.05	4.50	5.05	6.67	7.88
Temperature, K	453	473	493	513	533

### Activation Energy and Thermodynamics of Hydro-de-aromatization Process

The activation energy for the hydro-de-aromatization reactions was calculated by using Arrhenius equation, which satisfies the relation between rate constant and the reaction temperature (Levenspiel, 1972).

$$k = A \exp\left(\frac{-E^*}{RT}\right) \quad (8)$$

A plot of  $\ln k$  versus  $1/T$  gives a straight line with a slope equal to  $-E^*/R$  from which the activation energy was calculated, as shown in **Fig. (3)**.

Activation energy value (17.2 kJ/mole) is in a good agreement of activation energies of the de-metalization reactions of various crude oils and fractions reported (Abbas, 1999, Hummadi, 1999 and Mohammed and Abbas, 2001). The de-aromatization reaction then relatively temperature-insensitive due to its relatively low activation energy (Levenspiel, 1972).

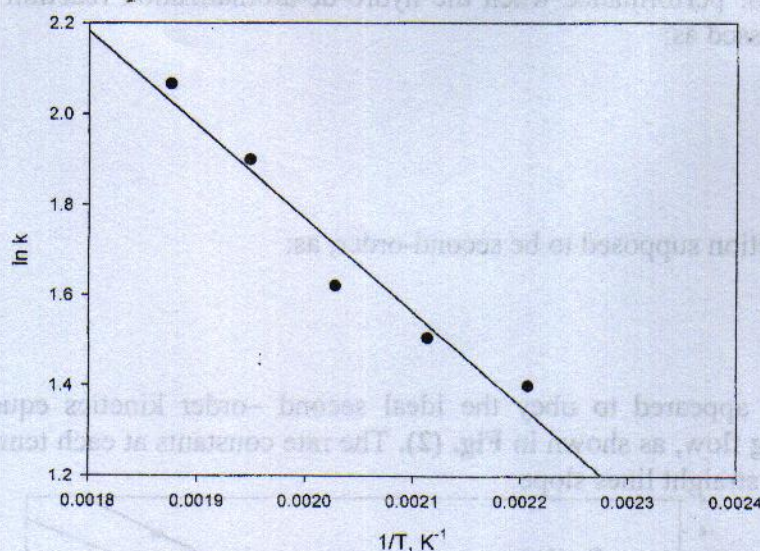


Fig. (3).  $\ln k$  versus  $1/T$  of second-order model for hydro-de-aromatization (Arrhenius plot).

The activation enthalpy and entropy for the hydro-de-aromatization reactions were calculated by using the following equation, which was obtained from the absolute rate theory (Bond, 1974)

$$k = \frac{KK_B T}{h} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-\Delta H^*}{RT}\right) \quad (9)$$



A plot of  $\ln(k/T)$  versus  $1/T$  (Fig. 4) gives a straight line with a slope equal to  $-\Delta H^*/R$  and intercept of this line equal to  $\ln((KK_B/h) + \Delta S^*/R)$ , then the activation enthalpy and entropy can be calculated. The results of these calculations are summarized in **Table (4)**.

Table (4). Calculated energy, enthalpy and entropy of activation for hydro-de-aromatization.

$E^*$ , kJ/mole	$\Delta H^*$ , kJ/mole	$\Delta S^*$ , J/mole K
17.2	13.1	-16.9

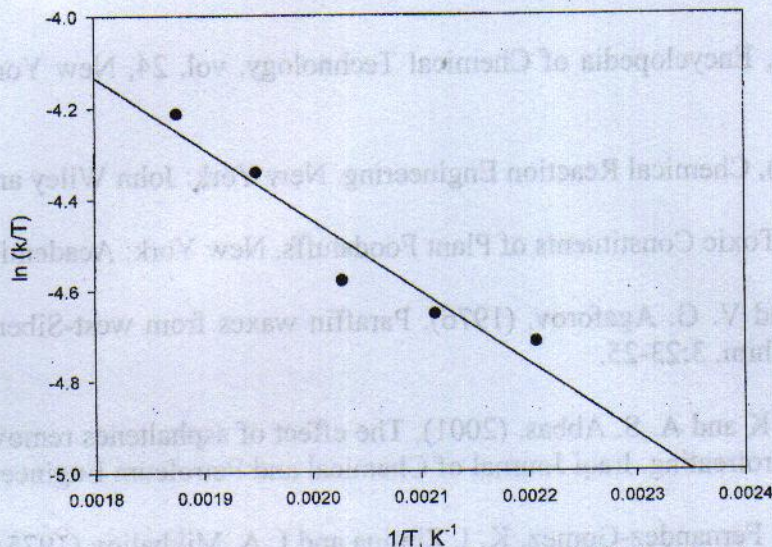


Fig. (4).  $\ln(k/T)$  versus  $1/T$  of second-order model for hydro-de-aromatization.

**CONCLUSIONS**

- 1-Aromatic removal from Iraqi paraffin wax (Basrah origin) by hydrotreating is between 50 at 4.2  $h^{-1}$  LHSV and 453 K up to 93 % at 0.5  $h^{-1}$  and 533 K.
- 2-The removal of aromatic hydrocarbons due to hydrotreating process is increasing with temperature and with decreasing LHSV in the range of 0.5 - 4.2  $h^{-1}$  LHSV and temperature of 453 - 533 K.
- 3-The hydro-de-aromatization reaction is obey second-order kinetics with rate constant ranging between 4.05 (wt%  $h^{-1}$ ) at 453 K to 7.88 (wt%  $h^{-1}$ ) at 533 K.
- 4- Activation energy, enthalpy and entropy of the hydro-de-aromatization are 17.2 kJ/mole, 13.1 kJ/mole and -16.9 J/mole K.

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## NOMENCLATURE

A	Frequency factor, (wt% h) <sup>-1</sup>
C <sub>A</sub>	Total aromatic content, wt%
C <sub>b</sub>	Benzene hydrocarbons content, wt%
C <sub>n</sub>	Naphthalene hydrocarbons content, wt%
C <sub>p</sub>	Phenanthrene hydrocarbons content, wt%
CW	Wax dissolved in isooctane, kg/m <sup>3</sup> (g/l)
D	Absorbency
d	Thickness of layer, m (cm)
E	Energy, J/mole
h	Plank's constant, 6.6262*10 <sup>-24</sup> J/s
H	Enthalpy, J/mole
HD	Hydrotreating process
k	Second-order rate constant, (wt% h) <sup>-1</sup>
k	Specific extinction coefficient
K	Transmission coefficient
K <sub>B</sub>	Boltzmann constant, 1.3806*10 <sup>-23</sup> J/K
LHSV	Liquid hourly space velocity, h <sup>-1</sup>
LSC	Liquid-solid chromatography





R	Universal gas constant, 8.314 kJ/mole K
S	Entropy, J/mole K
T	Reaction temperature, K
UV	Ultra violet

**Greek Letters**

$\Delta$	Change
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**Subscripts**

F	Feed
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**Superscripts**

*	Activation
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