EFFECT OF OPERATING CONDITIONS ON AROMATIC CONTENT AT BASRAH CRUDE OIL HYDROTREATING

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ABSTRACT

In Trickle Bed Reactor Basrah crude oil was hydrotreated using a common hydrotreating catalyst (Co-Mo/γ-Al_2O_3) . The operating conditions of this treating was, temperature (600 - 675 K) , Liquid hourly space velocity (LHSV) (0.6 - 1.9 hr^{-1}) , constant pressure (3 Mpa) and H_2/Oil ratio 300 L/L were performed .

Experiments results show that aromatic content was reduced as temperature increases and LHSV decreases, as well as the aromatic saturation were greatly enhanced at the same condition .

KEY WORDS

Destructive hydrotreating, hydrogenation, hydrocracking

INTRODUCTION

Crude oil is a very complex material, it consist mainly from different hydrocarbon compounds [1].

Market demands for different crude oil derivatives was greatly increases, the average consumption of different fuel like Gasoline, Kerosene, Jet fuels and others is 40 – 50 % from crude oil consumption and in 2000, the world wide consumption exceeding 70 % , according to that the high quality distillate production because a vital matter[2,3].

Aromatic compound is a cyclic unsaturated hydrocarbon, consist of single ring like (Benzene and Toluene) , two rings like (Naphthalene) , three rings like (Antharasene) or multi ring like (Pyrene) .

This type of hydrocarbon is one of the main compounds at which crude oil and it's derivatives consist of, for example benzene and toluene is the one of compound at which gasoline contain, kerosene contain a naphthalene, higher aromatic or polyaromatic is the formed or exist in higher boiling point petroleum derivative like fuel oil and as a rule of thumb, the quantity of aromatic compound proportion directly to the molecular weight of petroleum cuts [1,4] .

Many authors study the relation of aromatic content with sulfur, temperature and other variables .

A,reff [5] prove that the aromatic content increases as sulfur increases ,and shows that increasing the temperature during hydrotreating lead to saturate unstable hydrocarbon and become more stable for vacuum gas oil hydrotreating of Kirkuk crude oil.

In general the aromatic content increase in hydrocarbon beyond the gasoline, and it has a higher molecular weight which lead to increase the density of this cuts as fuel, in contrast the higher aromatic content in diesel oil reduce the quality of this cut due to higher time of autoignition. And due to their undesired properties, studies focus of many researcher, to reduce the aromatic content of different fuel by saturated this type of hydrocarbon in hydrotreating [4,6].

A hydrotreating is a catalyst process, used a proper catalyst to reduce or eliminate the sulfur compound, nitrogen compound, oxygen compound, metals and to saturate the unsaturated compounds like the oleffins to paraffins which lead to higher resistance to oxidant and the aromatic compounds to cyclic paraffins (naphthenic). These processes imply a hydrogen and higher temperature to accomplish the reaction kinetics[7].

This study conducted to reduce the aromatic content of Basrah crude oil by a hydrotreating process using a trickle bed reactor, with a bed of Co – Mo catalyst at 600 to 675 K temperatures, and 0.6 to 1.9 hr^{-1} LHSV, H_2/Oil ratio 300 L/L and constant pressure 3 Mpa .

Factors Affecting Hydrotreating

Hydrogen pressure is key role for obtaining a higher activity in reducing aromatic content that causes higher degree of aromatic saturation and reducing the coke formation [7,8].

A suitable hydrogen pressure depends on the feed type and hydrogen purity. Aromatic content increases as the density of feed increase, and this necessitate using a higher hydrogen pressure for complete or almost complete saturation and to restore the catalyst activity due to coke formation [9] .

Reaction temperature also another important factor. Increasing the reaction temperature increases also the possibility of coke formation due to heavy hydrocarbon dissociation .

Temperature increasing must be maintained to a certain limit, beyond this a thermal cracking will occur. Below 553 K a very slow reaction occur and over 683 K undesired reaction happened by thermal cracking of hydrocarbon producing a low value (low molecular weight) liquid and gases e.g. CH_4 ,C_2H_2 ,….. Etc [6,10] .

LHSV is another factor, LHSV is a ratio of volume treated per hour to catalyst volume and it is the inverse of resistance time will vary according to increasing the feed flow rate . A low LHSV lead to reduce the aromatic content [11] .

The produced gases must be kept for economic consideration . Increasing the H_2/Oil ratio lead to increase the hydrogen partial pressure and the mole fraction of high hydrocarbon gases [10,12] .

EXPERIMENTAL WORK

Feedstock

Basrah crude oil from Baiji refinery . Table (1) is a crude properties .

Catalyst

A Co-Mo/γ-Al_2O_3 was used for this process. Table (2) is the catalyst properties .

A 90 cm^3 of catalyst was discharged to the reactor (Trickle Bed Reactor) and dried at 393 K for 2 hour.

A 5.4 mm ceramic ball was putted in a two layer over and under the catalyst layer .

Catalyst activation was performed prior to feed introduction using a gas oil as splicing agent which contain 0.6 % CS_2 at 477 K and 2 Mpa hydrogen pressure, 2.66 hr^{-1} LHSV for 4 hr and at 573 K, 2 Mpa, 1 hr^{-1} and hydrogen flow 0.45 l/min for 16 hr .

Hydrotreating Process

The Hydrotreating runs were performed in a laboratory continuous high pressure unit employing an up-flow concurrent trickle bed reactor .

The reactor is stainless, and heats resisting steel with dimensions of 65 cm length, and 2cm diameter . The reactor was jacketed with five separately heat-controlled block shells in order to ascertain isothermal operation . The reactor products were cooled in a condenser-cooler and separator from unreacted hydrogen and the hydrocarbon gases by passing into a 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 in to the unit .

A calibrated micrometer was fitted in the pump to estimate the feedstock flow rate .

The hydrogen was fed to the reactor through a heated high pressure line . The unit was supplied with an electrical gas inlet flow sensor and hydrogen flow rate was estimated by standard calibrations with the electrical pulses. The catalyst bed was located between two bed of inert material with dimensions of 13.5cm length . Fig. (A) illustrates the flow diagram of the Hydrotreating unit .

Hydrotreating process was accomplished using a trickle bed reactor .The temperature range from 600 to 675 K , and 0.6 to 1.9 hr^{-1} LHSV, and in all the experiments pressure was maintained at 3 Mpa and 300 L/L H_2/Oil ratio . These ranges were taken from temperatures , and LHSV because of temperature above the ranges and degrease in LHSV below such ranges lead to reversible process that the process of dehydrogenation in addition to compounds cracking processes lead to formation of undesirable compounds , and under those ranges of temperatures and above ranges of LHSV , the reaction will be very little and doesn’t lead to the desirable results as approved by the previous and current practical experiments and stated in books and literatures .

While the reasons of pressure settlement at 3 Mpa , is due to the time age of the lab equipment used which doesn't allow use of ranges above this pressure and for safety purposes .

Reaction production was with drawn after reaching the steady state condition .

Deasphaltening Unit

The Basrah crude oil mixed with n-heptane as a solvent in 2-neck glass flask with an approximate volume of 250 cm^3. Solvent to oil ratio used 1-15 : 1 (volume to weight ratio) . Mixing was done by 12.5mm magnetic bar . Mixing time was varied between 0.25 to 4.0 hr .

The solution temperature was studied between 293 to 313 K and the required temperature was adjusted by water bath .

A high efficiency vertical condenser operating at total reflux was mounted on the mixing flask in order to decrease the solvent losses to a minimum .The condenser coolant was alcohol at temperature of 259 K and it was circulated through a cooling machine**.** Simplified Scheme of mixing system is shown in fig. (B) .

In order to filter the solvent-oil solution in a reasonable time a vacuum filtration unit was assembled, which consisted of, a filtration flask, Buchner funnel (90 mm in diameter) . A vacuum system including traps, condenser and a cooling machine, in order to avoid vacuum pump damage by the high volatility solvent .

Filtration paper was washed with the same solvent used at a reasonable amount and weighted after dried in an electric furnace maintained at 383 K for about 15 to 20 min . Schematic diagram of the Filtration system is illustrated in fig. (C) .

RESULTS AND DICUSSION

Figures (1– 4) show a decrease in the unsaturated aromatic compounds and an increase in the saturated compound with temperature increase because the unsaturated compound become saturated with hydrogen that increase of temperature leads to cracking of carbon bond and go apart from each other , and the forming parts become saturated with hydrogen.

The primary impact of hydrogen on the cyclic compounds is to open the ring and to be saturated directly while the multi-aromatic compounds of interfered ring react with hydrogen quicker than the mono-ring aromatic compounds and the reaction takes place in consequent steps that the rings become saturated and then each opens[13.5.1] . Also, increase of temperature leads to increase of activation energy of the materials leading to decomposition of the long compounds which concentrate in the heavy cuts which to an increase of Diffusion rate in the catalyst pores of active positions at which reactions of aromatic compounds saturation take place because their viscosity decrease[15.14] .

Figures (5 – 8) show decrease of the unsaturated aromatic compounds and increase of saturated compounds with decrease in the LHSV because increase of contact time i.e. increase of the reaction time between the reacting materials molecules on the surface of the catalyst to give the sufficient time to the saturation process because of increase of reaction time to decompose the unsaturated compounds due to the high temperature to saturate the unsaturated aromatic compounds and converting them in to saturated compounds like paraffins and cyclic paraffins[14,16] .

CONCLUSSIONS

1. Aromatic content reduction depends mainly on temperature and LHSV .
2. In the case of temperature increasing and LHSV decreasing aromatic content will reduce by increasing the aromatic saturation a saturated compounds like normal and cyclic paraffins .

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Table (1) Properties of Basrah crude oil

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Properties	**Value**
Sulfur content (wt %)	1.95
Specific Gravity at 15.6 ^{0}C	0.8560
API	33.6
Viscosity at 40 ^{0}C (cSt)	6.9
Pour point ^{0}C	-36
CCR (wt %)	4.1
Vanadium content (wt. ppm)	23.90
Nickel content (wt. ppm)	16.41
Ash content (wt %)	0.009

Table 2 Properties of catalyst commercial catalyst (CO-MO/γ-Al_2O_3)

Chemical specification	**Value**
MoO_3 (wt %)	15
NiO (wt %)	3
SiO_2 (wt %)	1.1
Na_2O (wt %)	0.07
Fe (wt %)	0.04
SO_2 (wt %)	2
Al_2O_3	Balance
Physical specification	**Value**
Form	Extrude
Surface area m^2/g	180
Pore volume cm^3/g	0.5
Bulk density g/cm^3	0.67
Mean particle diameter mm	1.8

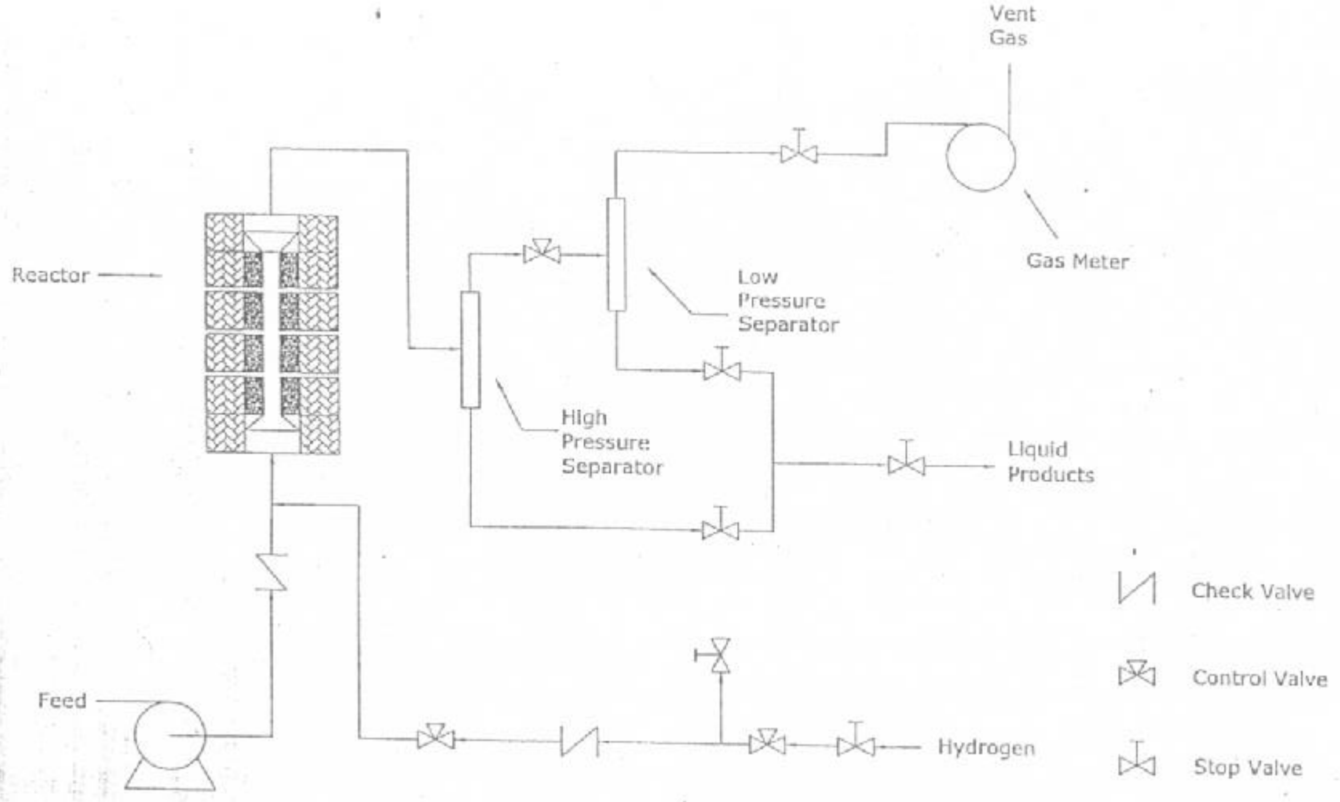

Fig.(1) Flow diagram of pilot hydrocracking unit

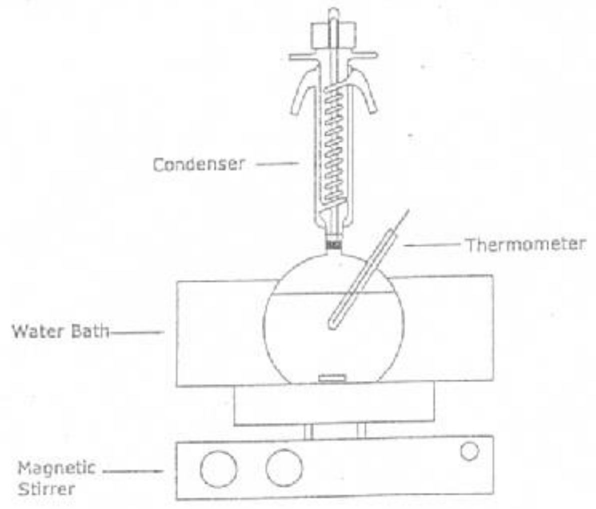

Fig. (B) Scheme for mixing unit

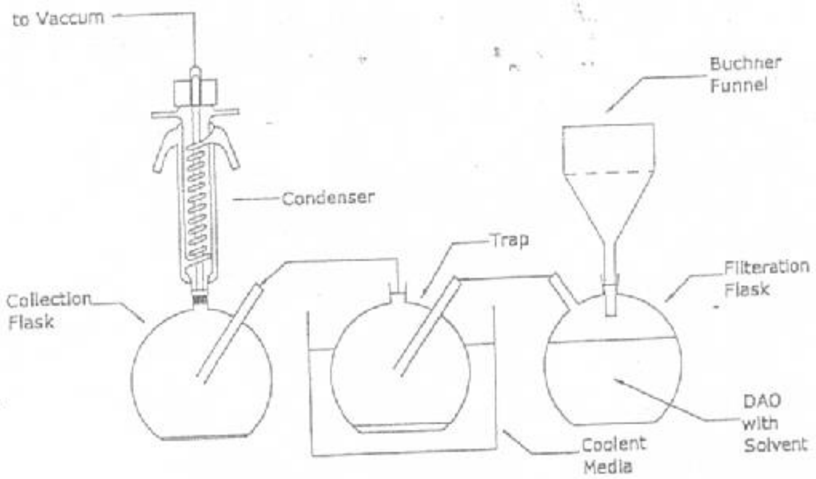

Fig. (C) Scheme for filtration unit

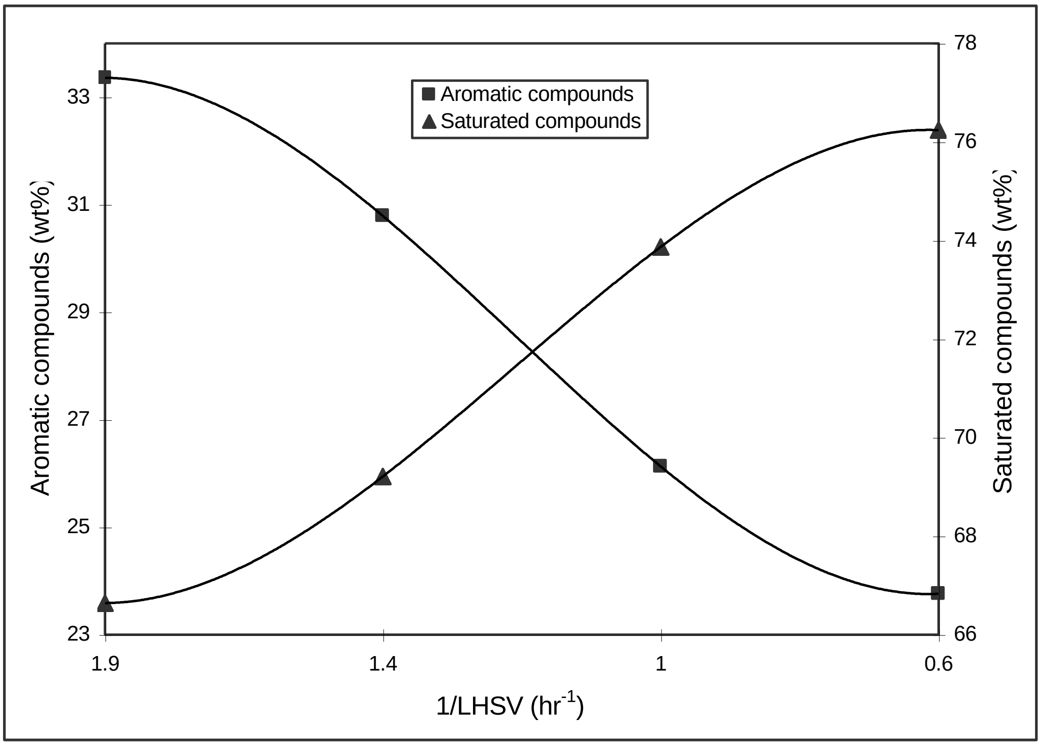

Fig. 1 Effect of LHSV on the aromatics and saturates content of hydrotreated products at 600 K

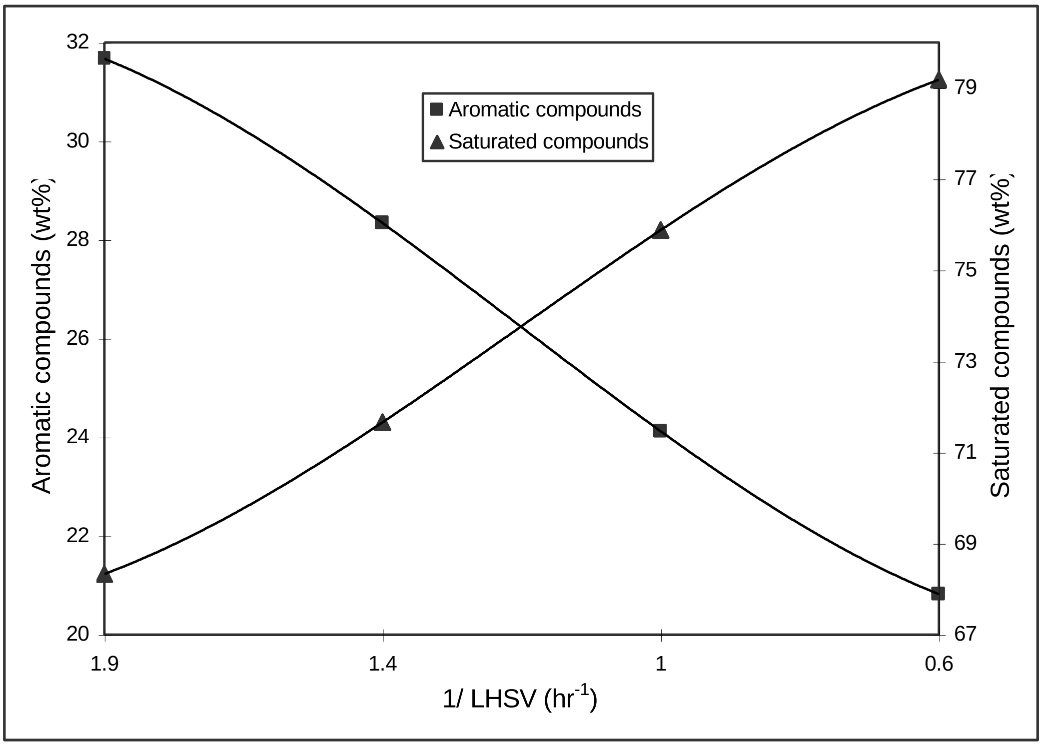

Fig. 2 Effect of LHSV on the aromatics and saturates content of hydrotreated products at 625 K

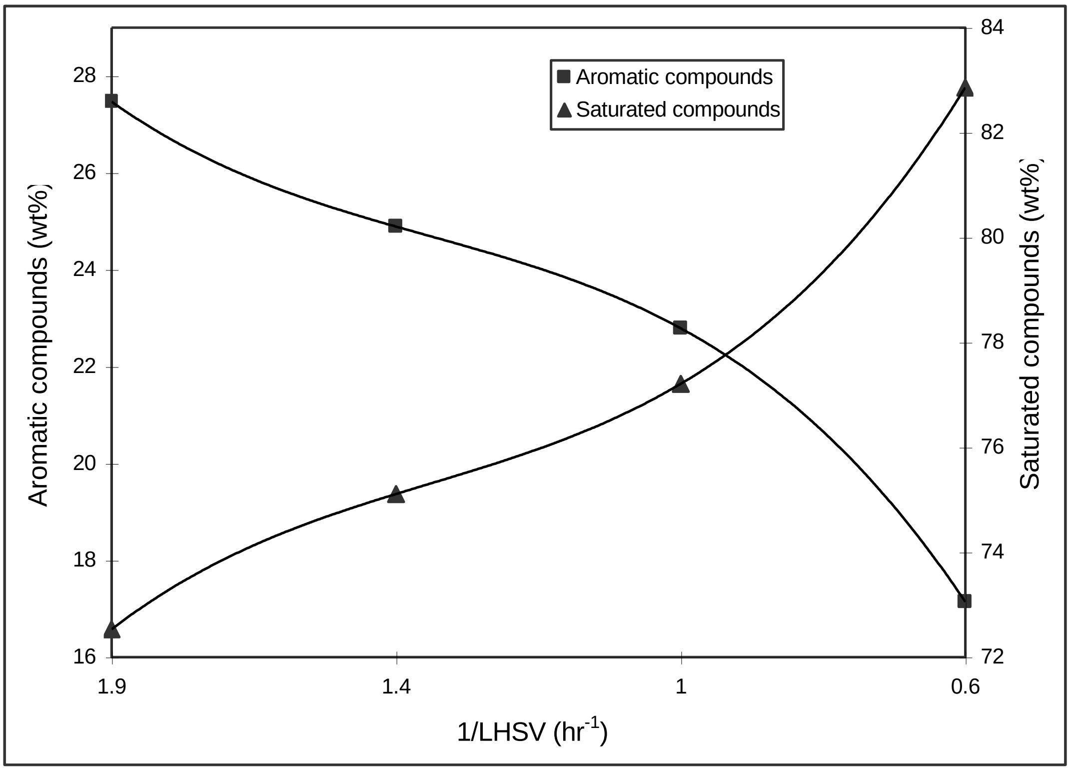

Fig. 3 Effect of LHSV on the aromatics and saturates content of hydrotreated products at 650 K

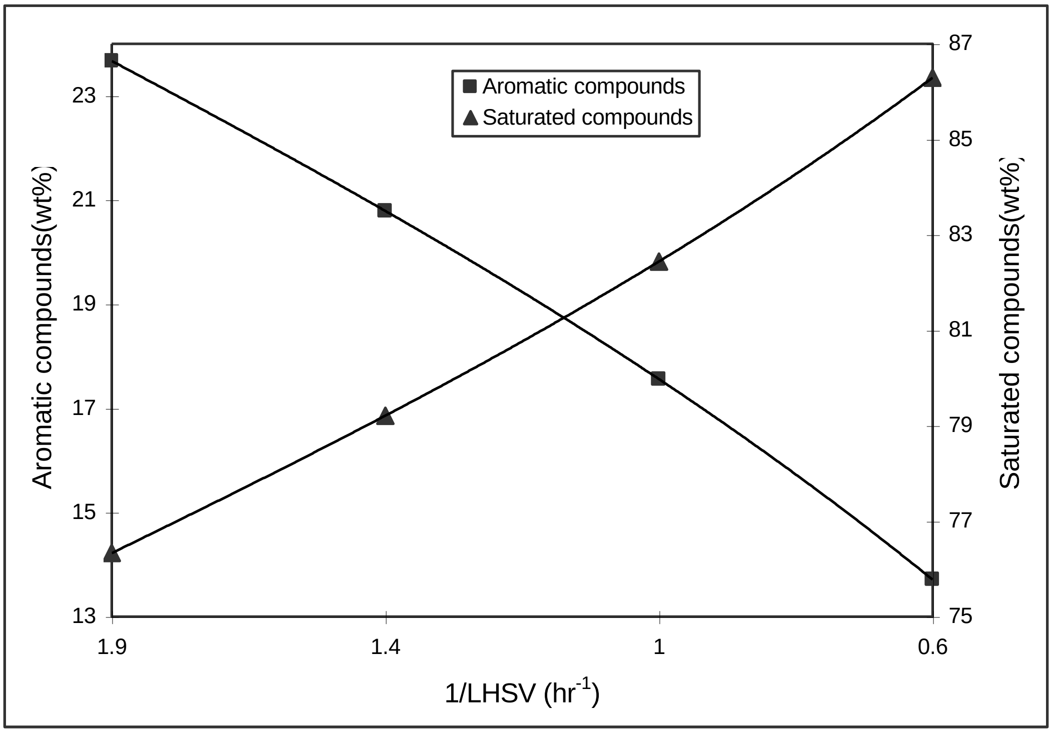

Fig. 4 Effect of LHSV on the aromatics and saturates content of hydrotreated products at 675 K

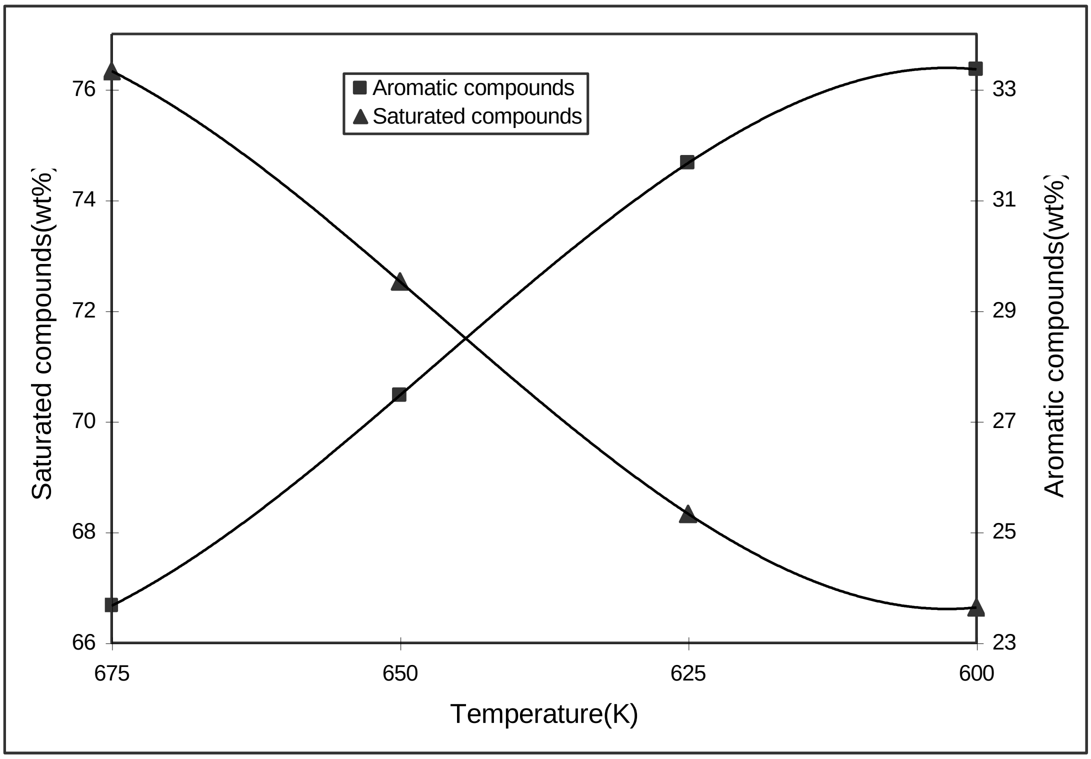

Fig.5 Effect of reaction temperature on the aromatics and saturates content of hydrotreated products at 1.9 hr^{-1}

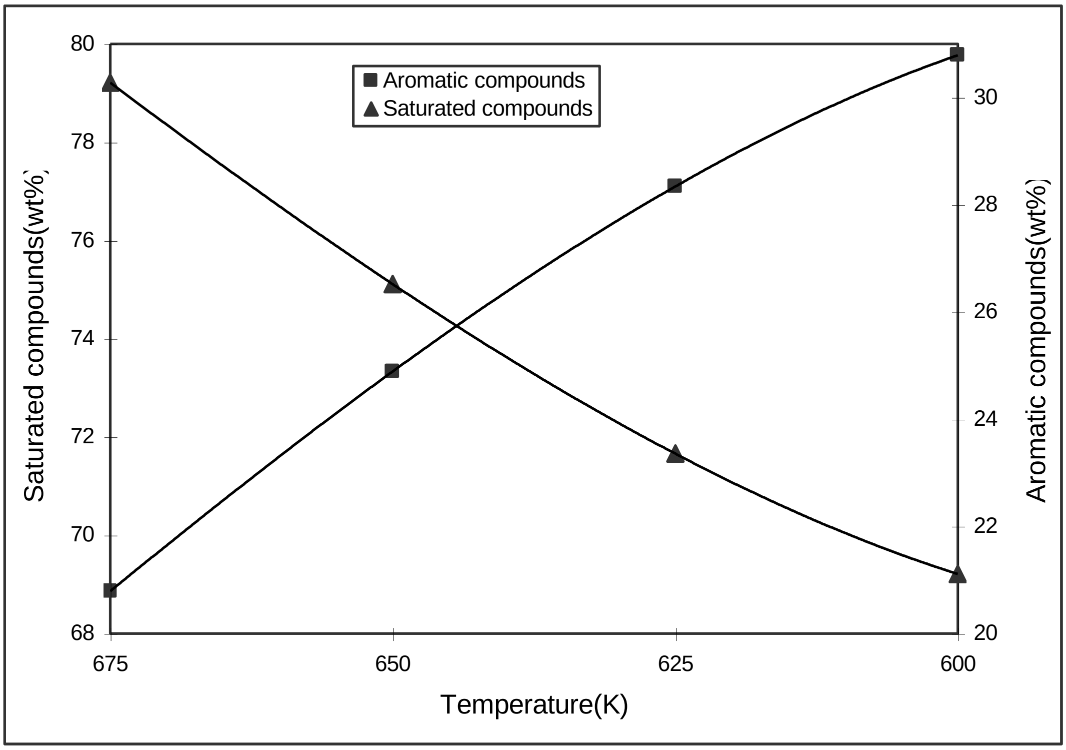

Fig.6 Effect of reaction temperature on the aromatics and saturates content of hydrotreated products at 1.4 hr^{-1}

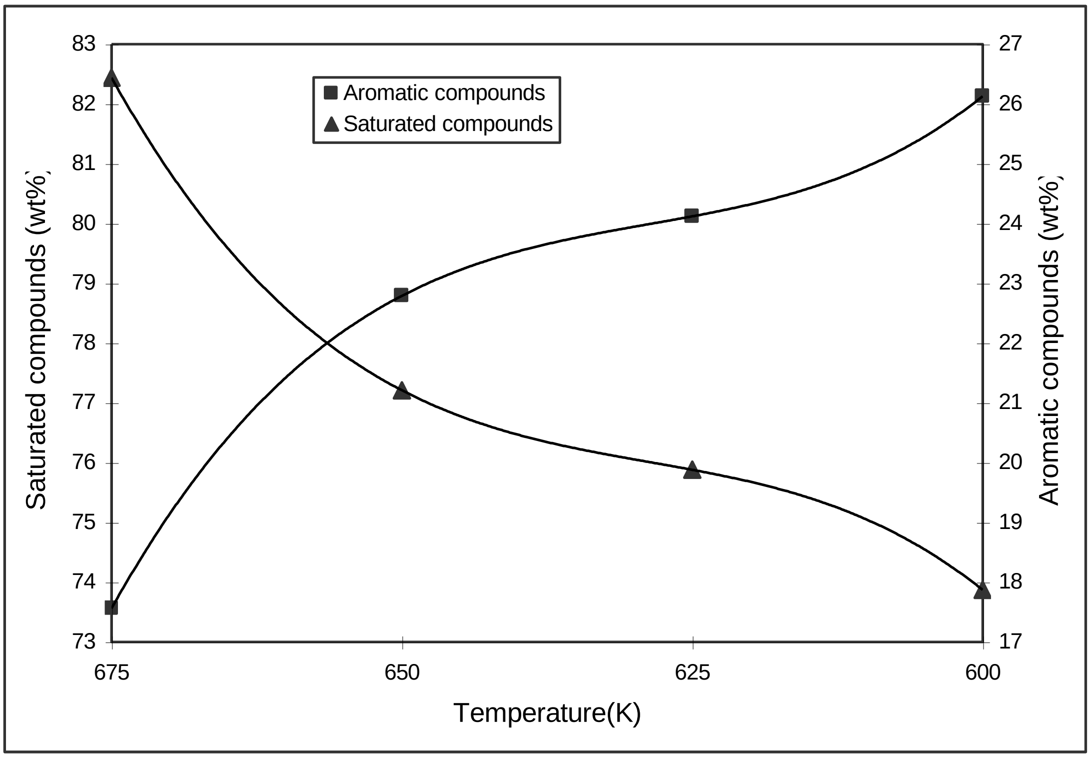

Fig.7 Effect of reaction temperature on the aromatics and saturates content of hydrotreated products at 1 hr^{-1}

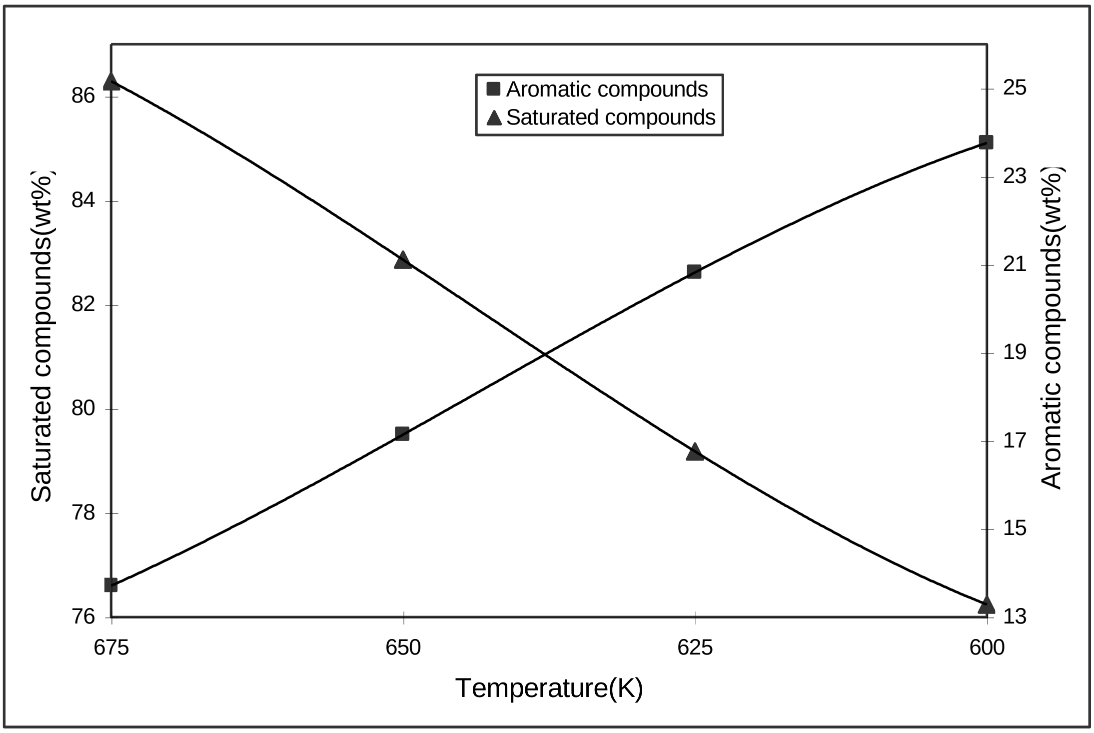

Fig.8 Effect of reaction temperature on the aromatics and saturates content of hydrotreated products at 0.6 hr^{-1}

تأثير الظروف التشغيلية على المحتوى ألأروماتي خلال المعاملة الهيدروجينية لنفط خام البصرة

أيسر طالب جارالله
قسم الهندسة الكيمياوية – جامعة تكريت

الخلاصة

تم معاملة نفط خام البصرة بالهيدروجين في مفاعل ثلاثي ألأطوار باستخدام الكوبلت – مولبيدنيوم المحمول على ألألومينا كعامل مساعد . حدود درجات حرارة التفاعل كانت من 600 إلى 675 كلفن وحدود سرع السائل الفراغية كانت من 0.6 إلى 1.9 ساعة$^{-1}$ ، علماً أن التفاعل كان تحت ضغط هيدروجيني ثابت مقداره 3 ميكاباسكال وباستعمال نسبة هيدروجين إلى المغذي 300 لتر/لتر.

تبين من النتائج ان المحتوى ألأروماتي يقل بارتفاع درجة الحرارة وانخفاض سرعة السائل الفراغية يقابله زيادة تشبع المركبات ألأروماتية خلال عملية المعاملة الهيدروجينية لنفط خام البصرة.

الكلمات الدالة

التشبع الهيدروجيني ، الهدرجة ، تشبع المركبات ألأروماتية