

EFFECT OF OPERATING CONDITIONS ON HYDRODESULFURIZATION OF VACUUM GAS OIL

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ABSTRACT - The study deals with the hydrotreating of vacuum gas oil with boiling range (611-833K) using trickle bed reactor and a commercial cobalt – molybdenum on alumina as a catalyst with temperature range (583-643K) , liquid hourly space velocity range (1.5-3.75 hr⁻¹) , hydrogen to oil ratio about 250 lt / lt , and hydrogen pressure kept constant at 3.5 MPa.

The results showed that the aromatic content of vacuum gas oil decreased while sulfur removal increased with increasing temperature and decreasing space velocity. The properties, viscosity, density, flash point, and carbon residue of the products are decreased with temperature increasing but the aniline point did the otherwise.

KEY WORDS: Hydrodesulfurization, Vacuum Gas Oil, Trickle Bed Reactor.

1. INTRODUCTION

Hydrotreating process plays an important role in the petroleum refinery. It is a catalytic conversion and removal of organic sulfur, nitrogen, oxygen compounds and metals from petroleum fractions and residua at high hydrogen pressures and temperatures accompanied by hydrogenation of unsaturated hydrocarbons and cracking of the high molecular weight to lower molecular weight. Indeed, hydrotreating capacity has been growing steadily (at about 6% per year since 1976) and represents today nearly 50% of the total refining capacity⁽¹⁾. The increasing application of hydrotreating can be ascribed to:

- i-**The ever decreasing availability of light, sweet crudes and thus increasing in fractions of heavy, sour crudes that must be processed.
- ii-**The trend to increase upgrading of feedstocks for improvement of downstream processing such as catalytic reforming and catalytic cracking⁽²⁾.

The hydrodesulfurization of petroleum fractions has long been an integral part of refining operations, and in one form or another, hydrodesulfurization is practiced in every modern refinery⁽³⁾.

The technology of the hydrodesulfurization process is well established, and petroleum feedstocks of every conceivable molecular weight range can be treated to remove sulfur. Thus, it is not surprising that an extensive knowledge of hydrodesulfurization has been acquired along with the development of the process over the last few decades. However, most of the available information pertaining to the hydrodesulfurization process has been obtained with the lighter and more easily desulfurized petroleum fractions; but it is, to some degree about the hydrodesulfurization of the heavier feedstocks such as the heavy oil, vacuum gas oil and residua. On the other hand, the processing of the heavy oils and residua present several problems that are not found with distillate processing and which require process modifications to meet the special requirements that are necessary for heavy feedstock desulfurization⁽³⁾.

Hydrodesulfurization of heavy oils with demands of rapidly increasing low sulfur fuel oil markets is one of the major technical and economic challenges facing the refining industry during this decade. One route to low sulfur oil production is vacuum gas oil (VGO) desulfurization. Atmospheric distillation residuum is first fractionated to vacuum gas oil and residuum. The sulfur content of the vacuum gas oil is then significantly reduced by means of catalytic hydrodesulfurization. This process has the advantage of being relatively inexpensive. Feedstocks to this process may include virgin and visbreaker vacuum gas oil, thermal and catalytic cycle, and cooker gas oil^(4,5).

The present study conducted according to contract with North Refineries Company - Baji and deals with the effect of operating conditions on hydrodesulfurization of vacuum gas oil using trickle bed reactor.

EXPERIMENTAL WORK

The feedstock used in present work is a vacuum gas oil (VGO) with boiling range (611-833K) and prepared by blending the fractions of light VGO (611-650K), medium VGO (650-690K), heavy VGO (690-727K), and very heavy VGO (727-833K) with the volume percentages 13.67, 21.67, 27, 37.66 respectively. The properties of the VGO used are given in Table (1).

The catalyst used is a commercial cobalt-molybdenum on alumina (Co-Mo/Al₂O₃) type and its properties are shown in Table (2). The catalyst presulfided to promote its activity by

charging 120 cm³ of the fresh catalyst to the hydrodesulfurization reactor after drying at 393K for two hours and using a solution of 0.6 vol.% of CS₂ in a commercial gas oil. The first 4 hours of activation carried out at 21 bar and 477K with 4 hr⁻¹ liquid space velocity and no hydrogen flow. The next step of the activation was 16 hr with the following conditions: temperature, 573K, LHSV, 1 hr⁻¹, pressure, 2.1 MPa and hydrogen to oil ratio of 200 lt/lt.

The sulfur content of the feedstock was determined using bomb method ASTM: D 129-64 and the groups' composition of VGO are determined by liquid- solid chromatography using silica gel as the absorbent. The chromatography column with 25mm in diameter was packed to a height of 500mm silica gel and about 2gm of sample was introduced into the column. The chromatography column is shown in Fig. (1). The saturated fraction was eluted from column using 150 cm³ of n-hexane, then the aromatics fraction was eluted by 200 cm³ of benzene. Finally, the polar aromatics fraction eluted from the column with 150 cm³ of methanol-benzene mixture (20/80) by volumes. Table (3) shows the sulfur, aromatics, and saturated fractions distribution in feedstock fractions.

The hydrodesulfurization (HDS) runs performed in a laboratory continuous high pressure unit employing an up-flow co-current trickle bed reactor. The reactor made of stainless steel with dimensions are 65cm length and 2cm diameter and jacketed with five separately heat-controlled block shells in order to keep a certain isothermal operation. The reactor products are cooled in the condenser and separated from unreacted hydrogen , H₂S and the hydrocarbon gases passing through a high and low pressure separators. The gases then vented to the exterior through a gas flow meter. The unit supplied with a high pressure dosing pump to introduce the feedstock to the reactor. A calibrated micrometer was fitted with pump to estimate the feedstock flow rate. The hydrogen fed to the reactor from a hydrogen cylinder through a heated high pressure line. The hydrogen flow rate estimated by electrical gas inlet flow sensor using standard calibrations with the electrical pulses.

The catalyst bed in the reactor was located between two beds of inert material (balls of porcelene) with dimensions of 13.5cm length. Fig.(2) shows the flow diagram of the HDS unit.

The HDS experiments of the VGO were carried out at temperature range of (583-643K) over liquid hourly space velocity (LHSV) ranging from 1.5 to 3.75 hr⁻¹ , hydrogen pressure kept constant at 3.5 MPa , and hydrogen to feed ratio approximately 250 lt/lt was employed through the experiments and when the steady-state operation was established , the products were collected.

The hydrotreated products fractionated by laboratory distillation unit. The unit consists mainly of round bottom flask, distillation column, still head distillate receivers, reflux condenser, and vacuum system. The unit is shown in Fig. (3). The distillation unit operated at atmospheric pressure up to the distillation temperature of 611 K, then the distillation unit system connected to the vacuum pump through a vapor trap to continue the distillation at a vacuum pressure as low as 0.5 mm Hg. A magnetic valve connected to the reflux timer was used to obtain the desired reflux ratio. The reflux ratio was 3:1 for distillation temperature up to 611 K and 1:1 for the remainder fractions. The specific gravity, flash point, kinematic viscosity, carbon residue of the feedstock and the products were measured using IP 120/64, IP15/57, IP319/75, and IP 3/66 standards methods respectively.

RESULTS AND DISCUSSION

The hydrodesulfurization of vacuum gas oil in a fixed catalyst bed reactor is a complex process and many variables affect the extent of sulfur removal. The main variables are temperature, pressure, LHSV, and hydrogen to oil volumetric ratio. Through the present study, the hydrogen pressure and the hydrogen to oil ratio kept constant.

The results show that the sulfur content and sulfur removal of hydrotreated product are increasing with increasing temperature and decreasing LHSV as illustrated in Figs (4-6). The results obtained are agreed with the other studies for the HDS^(6, 7, 8, 9). The increasing of sulfur removal at high reaction temperature may be attributed to several reasons. Firstly, the unreactive sulfur compounds which most properly belong to thiophene derivatives become activated enough to react with hydrogen and secondly, the aromatic compounds are decomposed to smaller one which can more easily diffuse into the catalyst micro and mesopores and reach the inner active sites where the desulfurization reaction mainly occurs⁽¹⁰⁾. Thus, the upper temperature value is limited by the undesirable side reactions such as hydrocracking and thermal cracking reactions which are expected to occur at high temperature.

The contact time between the reacting fluids and catalyst decreases with increasing the LHSV and this leads to the extent of sulfur removal decrease with increasing LHSV.

The distribution of sulfur content in the hydrotreated fractions, LVGO, MVGO, heavy VGO, and very heavy VGO studied and the results shown in Fig. (7). Noted that the sulfur content of hydrotreated fractions lowered with decreasing LHSV at the temperature used (643K).

Several classes of reactions occur simultaneously in HDS process which includes hydrodenitrogenation (HDN), hydrodeoxygenation (HDO), hydrocracking, and hydrogenation⁽¹¹⁾.

Figs. (8) and (9) show the decreasing of aromatic compounds and increasing of saturated compounds in the hydrotreated product with increasing reaction temperature and decreasing of LHSV due to the increasing of the rate of hydrogenation of aromatics and increasing the contact time as mentioned by Girgis⁽¹¹⁾.

The effect of hydrotreating temperature and LHSV on aniline point of the hydrotreated product shown in Figs. (10) and (11). The aniline point increases with temperature increasing and LHSV decreasing due to the increasing of the rate of hydrogenation reaction which causes decreasing in aromatic content. The viscosity, flash point, density, and carbon residue decrease with increasing in temperature and reaction time as shown in Figs. (12–19). The decreasing in these properties is due to the increase in hydrogenation and hydrocracking reactions.

CONCLUSIONS

- 1- Sulfur removal from vacuum gas oil produced in Baji refinery is highly dependent on temperature and LHSV variation within the range of studied operation.
- 2- Hydrodesulfurization rate is generally higher than hydrogenation rate at conditions covered by this investigation.
- 3- Ability to produce different grades of oils is possible with 1.124, 0.98, 0.813, and 0.612 wt % sulfur content from the hydrotreated VGO.

REFERENCES

1. Mc Culloch, D. C., "Catalytic Hydrotreating in Petroleum Refining", in Applied Industrial Catalysis, Ed.B.E. Leach, Academic Press, Vol.1, pp: 69; 1983.
2. Bartholomew C.H., "Catalyst Deactivation in Hydrotreating of Residua", in Applied Industrial Catalysis, Ed.B.E. Leach, Academic Press, Vol. 1, pp: 64; 1983.
3. Speight, J. G., "The Desulfurization of Heavy Oils and Residua", 1981.
4. Hobson, G.D., "Modern Petroleum Technology", 5th Ed., Part I, 1984.
5. Antos, G.J and Wang, L., "Successful Commercial Hydrocracking Catalysts Tools and Methodologies", 2000.

6. Leong, T. K., Mohamed, A. R. and Bhatia, S., "Hydrotreatment of Diesel Oil over Sulfided Co-Mo/Al₂O₃ and Ni-Mo/Al₂O₃ Catalysts", Hydrocarbon Processing, 1999.
7. Vicic, D. A. and Jones, W. D., "Hydrodesulfurization of Thiophene and Benzothiophene to Butane Ethylbenzene by a Homogeneous Iridium Complex", Organometallics., Vol. 16 ; pp:1912-1919; 1997.
8. Antonio Iannibbillo, Sergio Marengo, Geriando Burgio, Glancario Baldo, Silivo, and vito Specchia, Ind. Eng. Chem. Process Des. Dev.; Vol .24; pp: 531- 537; 1985.
9. Mann, R .S; Sambhi, L. S.; and Khulba, C .K. Ind.Eng.Chem.Res; Vol. 27, pp: 1788-1792; 1988.
10. Froment ,G .F. ; DePauw, G.A. and Vanrysselberghe, V., Ind. Eng. Chem. Res.; Vol. 33; pp: 2975 - 2988; 1994.
11. Grirais, M. J. and Gates, B. C.; Ind. Eng. Chem. Res. ,Vol. 30, pp: 2021-2058;1991.

Table (1) :The properties of VGO feedstock.

Specification	Value
Sp.gr.at 60/60 F	.
°API	.
Viscosity, cst, at 323 K 373 K	. 2.784
Pour point ,K	
Flash Point ,K	
Aniline point, K	
CCR ,wt.%	0.58
Sulfur content, wt.%	2.5

Table (2): The catalyst properties.

Chemical specification	Value Wt.%
MoO ₃	15.0
NiO	3.0
SiO ₂	1.1
Na ₂ O	0.07
Fe	0.04
SO ₄	2.0
Al ₂ O ₃	Balance
Physical specifications	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
Mean particle length mm	4

Table (3): The distribution of sulfur, aromatics, and saturated fraction distribution in VGO fractions.

Fractions	Fraction Wt %	Sulfur Wt %	Aromatic Wt %	Saturated Wt %
LVGO (611-650 K)	8	2.38	16	84
MVGO (650-690 K)	23	2.40	24	76
HVGO (690-727 K)	29	2.50	34	66
Very HVGO (727-833 K)	40	2.60	50	5

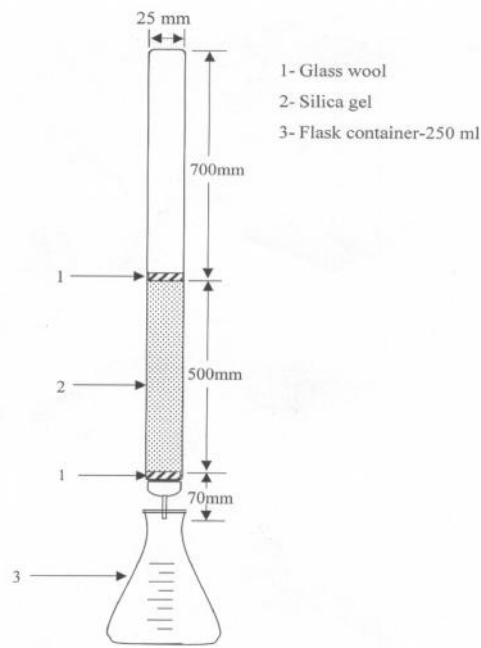


Fig. (1): Liquid-Solid chromatography column.

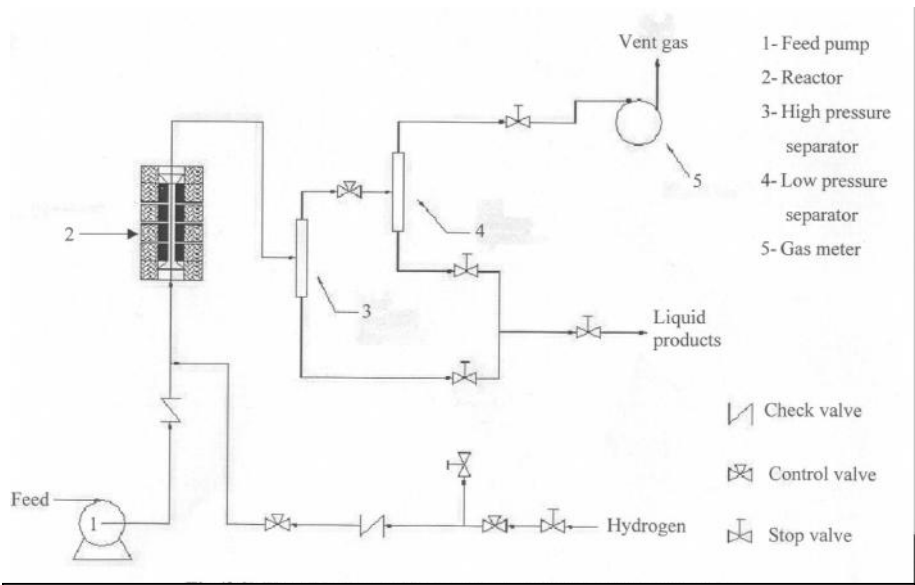


Fig. (2): Flow Diagram of Laboratory Hydrodesulfurization Unit.

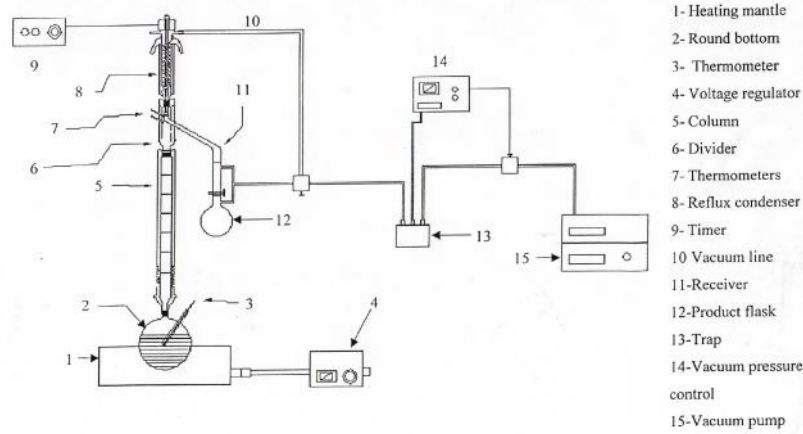
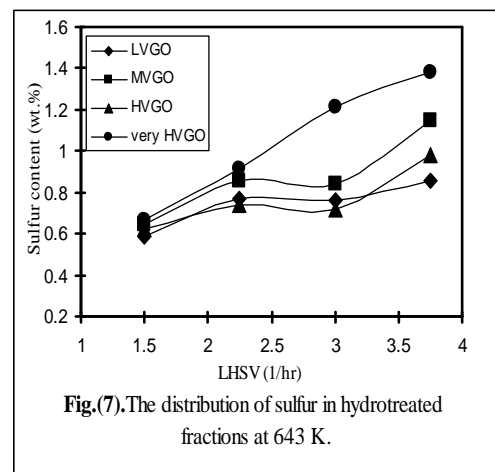
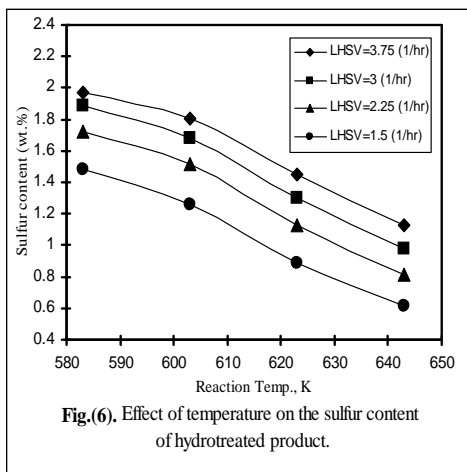
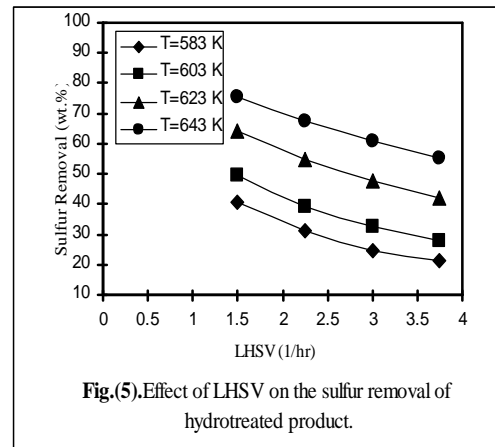
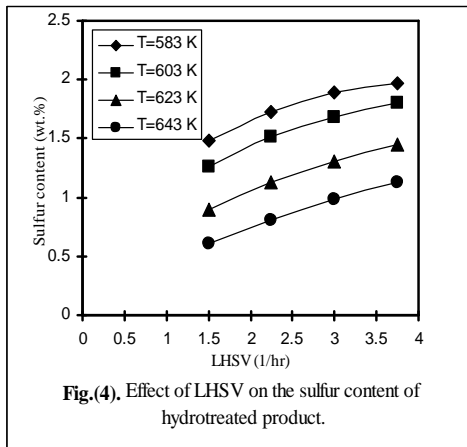


Fig.(3). Laboratory distillation unit.



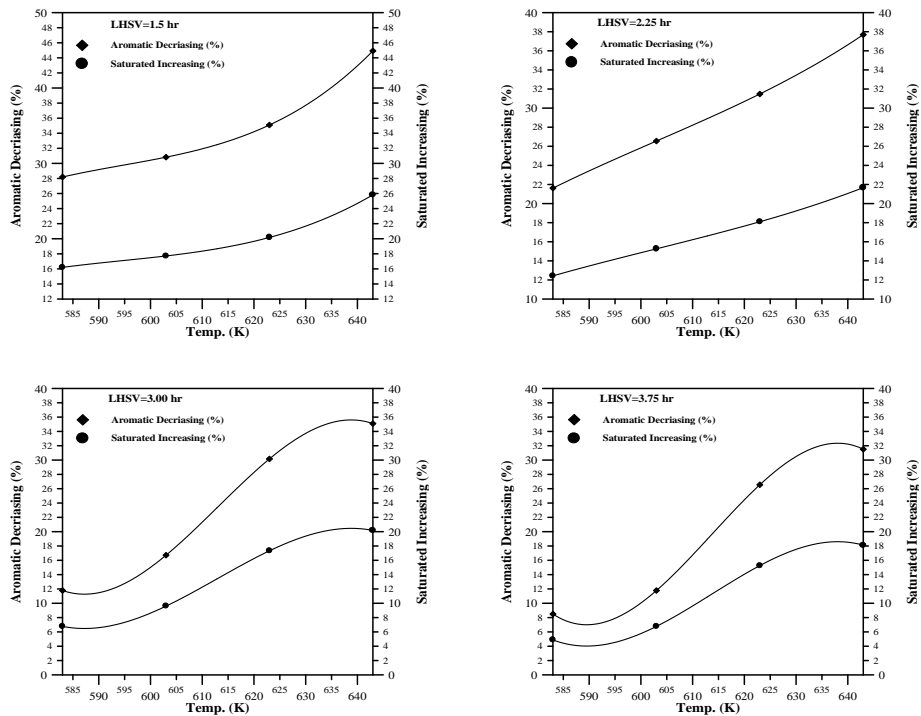


Fig. (8). Effect of LHSV on the aromatics and saturates content of hydrotreated products.

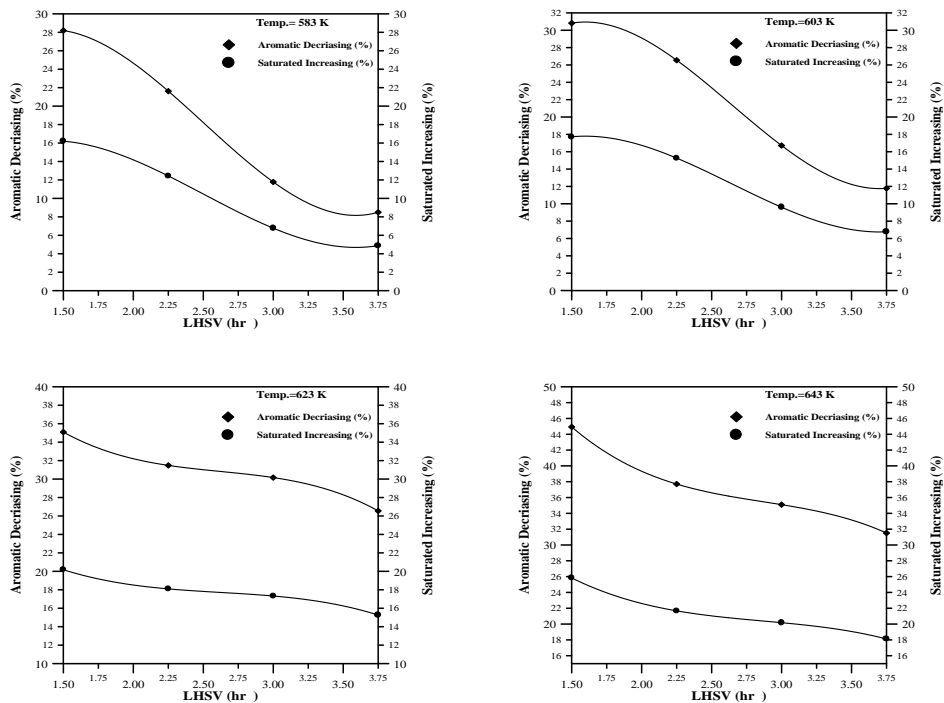
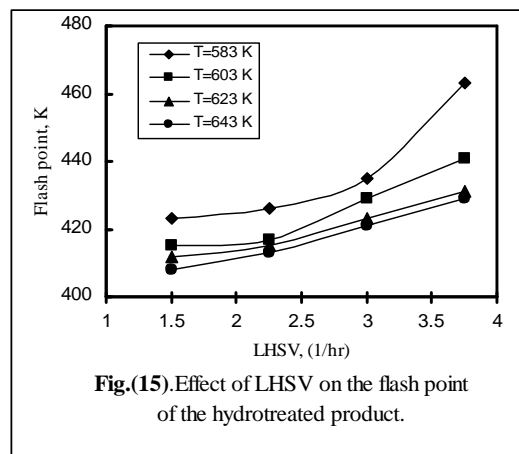
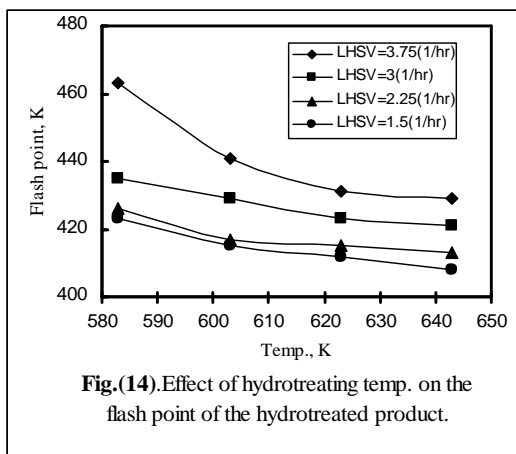
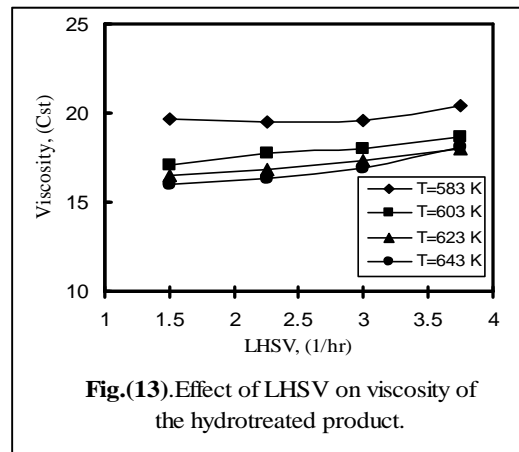
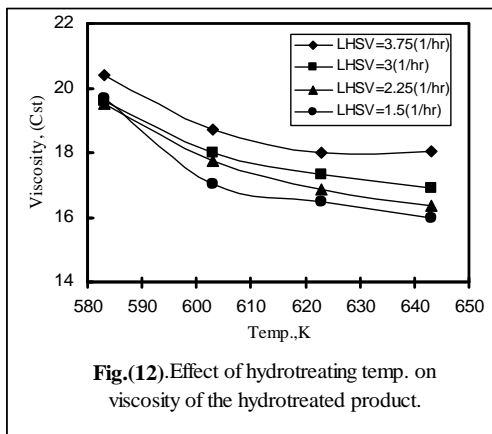
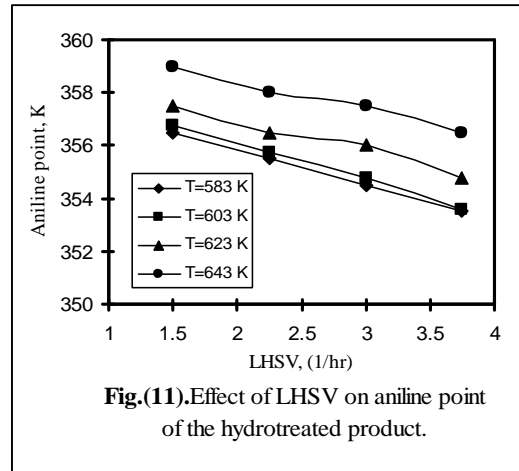
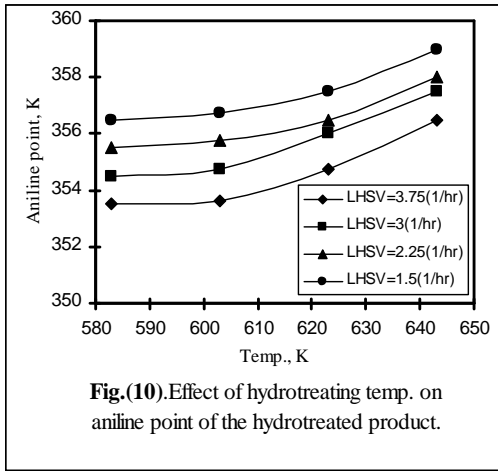
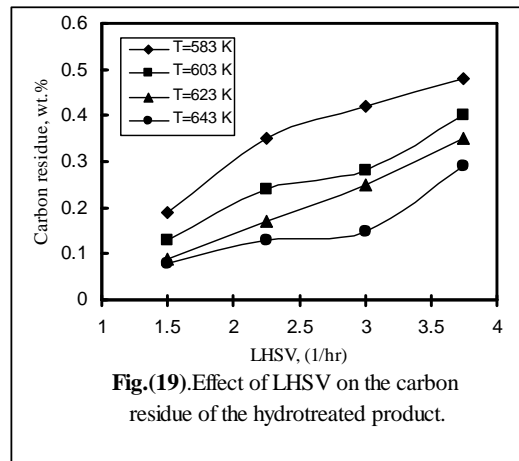
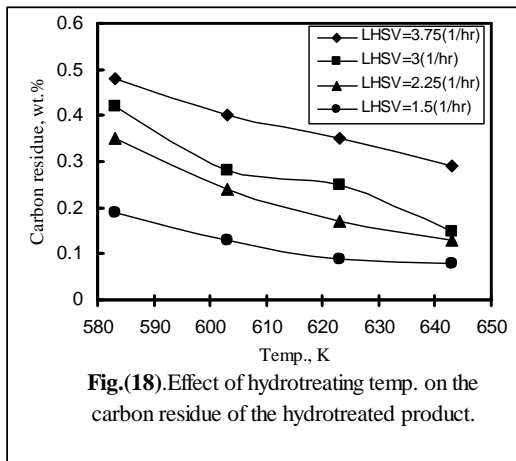
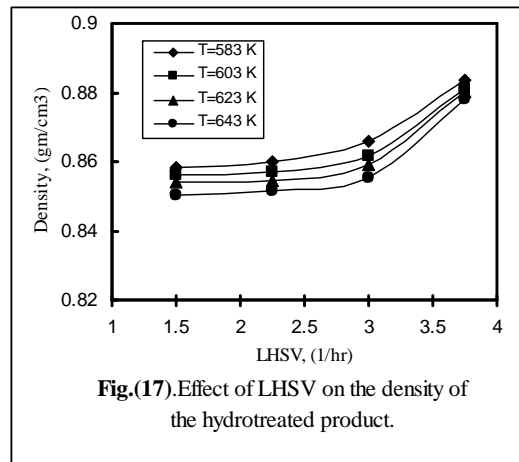
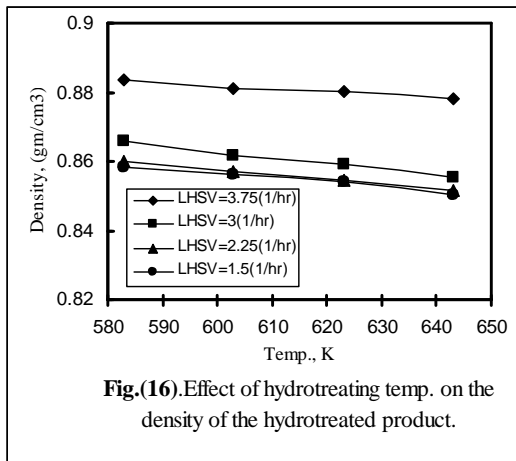


Fig. (9). Effect of temperature on the aromatics and saturates content of hydrotreated products.





تأثير الظروف التشغيلية على المعاملة الهيدروجينية لزيت الغاز الفراغي

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الخلاصة

لقد تمت الدراسة بموجب عقد مع شركة مصافي الشمال في بيجي و التي تتناول دراسة المعاملة الهيدروجينية لزيت الغاز الفراغي ذو مدى غليان (611 - 833) كلفن باستخدام المفاعل الخريبي (Trickle bed reactor) والعامل المساعد الصناعي كوبلت - موليبدنيوم (Cobalt - Molybdenum) المحمل على ثالث أوكسيد الألمنيوم ومدى درجات حرارة (583 - 643)؛ كلفن وسرعة سائل فراغية (1.0 - 3.75) ساعة⁻¹ ونسبة الهيدروجين الى الزيت حوالي (250) لتر / لتر وضغط (3.5) ميكا باسكال .

لقد بينت النتائج المستحصلة بان المحتوى الاوروماتي و نسبة الكبريت المزال تزداد مع زيادة درجة الحرارة وانخفاض السرعة الفراغية وان الخصائص للزوجية والكثافة و نقطة الوميض و المتخلف الكار بوني للنواتج ينخفض مع زيادة درجة الحرارة ألا أن نقطة الانبيلين عكس ذلك.

الكلمات الدالة: المعاملة الهيدروجينية، زيت الغاز الفراغي، المفاعل الخريبي.