CATALYTIC AROMATIZATION OF NAPHTHA USING DIFFERENT CATALYSTS

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ABSTRACT

Heavy Iraqi petroleum naphtha with average boiling point of 385K and 0.7388 specific gravity was tested with various types of prepared and commercial catalysts for the aim of production toluene and xylenes. The aromatization process carried out with prepared chromia-alumina catalyst promoted by potassium and cerium, and with commercial platinum-alumina catalysts promoted by rhenium and tin, in a fixed bed reactor.

The aromatization process carried out at a range of temperatures varied from 703 to 763K, liquid hourly space velocity varied from 0.2 to 0.5h-1, and atmospheric pressure.

The general behavior of aromatization process indicates that toluene and xylenes were increased with increasing temperature of reaction, while decreased with increasing LHSV.

Prepared chromia-alumina promoted with potassium and cerium catalyst gives conversion of n-heptane and n-octane to toluene (31% yield) and to xylenes (80% yield) respectively, while chromia-alumina promoted only with potassium gives maximum conversion of n-heptane and n-octane to toluene (15% yield) and to xylenes (50% yield) respectively. Commercial platinum-alumina catalysts promoted with tin gives maximum conversion of n-heptane and n-octane to toluene (42% yield) and to xylenes (63% yield) respectively. Any way, commercial platinum- alumina promoted with rhenium and the unpromoted catalysts gives very low conversions.

Keywords: Catalytic reforming , Aromatization of naphtha, BTX production.

INTRODUCTION

Toluene and xylenes are the most important aromatic compounds . They have wide range industrial applications. Prior to World War I, the main source of aromatics was coke ovens (coal conversion process, carbonization). As the demand for these aromatics are increases, petroleum naphthas became the main source for them.

Toluene is generally produced along with benzene, xylenes, and C_9 aromatics by catalytic reforming of C_6-C_9 naphthas. The resulting crude reformat is extracted, most frequently with sulfolane, to yield a mixture of benzene, toluene, xylenes, and C_9 aromatics, which are then separated by fractionation[1].Toluene was for the first time obtained from petroleum sources by subjecting narrow-cut naphthas containing relatively small amounts of toluene to thermal cracking.

The British Catarole process directed primarily to production of chemical intermediates (aromatics) rather production of high-octane fuels by catalytic reforming process. Also, although the Catarole process produces large amounts of aromatics, it produces them through a basically different mechanism than does catalytic reforming. In hydroforming, naphthenes are isomerized and dehydrogenated to aromatics in a relatively mild rearrangement process [2].

The availability of large quantities of hydrocarbons from petroleum industry makes it a logical source of raw materials for the production of aromatics .U.O.P Platforming process involves the continuous reforming of straight run and cracked gasolines in the presence of a supported platinum catalyst. One of the major reactions in the platforming is the formation of aromatic hydrocarbons. Thus, a plant which operates for the projection of motor fuel can operate equally

well for aromatic production. Some plants are being designed to operate intermittently for the projection of aromatics and motor fuel.

Historically, platinum and nickel on alumina have been used much earlier in hydrocarbon studies .Hydroforming reactions include dehydrogenation, isomerization, hydrocracking, and dehydrocyclization, dehydrogenation of alkyl substituted cyclohexanes is rapidly accomplished by platinum catalysts. Dehydrogenation of naphthenes results in a wide variety of aromatics, all which have blending RON above 100. Because cyclohexane derivatives are essentially paraffinic in nature and under conditions of commercial hydroforming are subject to hydrocracking as are members of the aliphatic group the more rapidly they are converted to aromatics, the less possibility there is for opening the naphthene ring, and there for the better is the aromatization selectivity. Isomerization activity in a hydroforming catalyst is important for two reasons [3,4], the first is the isomerization of cyclopentane derivatives to cyclohexane derivatives must be accomplished rapidly and selectively in order to maximize naphthene aromatization. The second is isomerization is also essential for achieving equilibrium distribution of paraffin isomers.

Selectivities of catalysts depend to some extent on the make – up of the feedstock. Alky cyclohexanes are readily converted to aromatics by all dehydrogenation catalysts. For the conversion of alkylcyclopentanes, on the other hand, there are large differences. Because alkylcyclopentanes require an isomerization step, their conversion to aromatics depends upon the isomerization activity of the catalyst. Aromatics also can be produced from paraffins by dehydrocyclization process, such as n-heptane and n-octane gives toluene and xylenes respectively [5, 6].

Tests with platinum-promoted catalysts indicated that the concentration chosen, 0.1% by weight, was about the optimum. Potassium was a strong promoter, depending on its concentration range with chromia-alumina catalysts. Cerium in the same range was even better than potassium.

The aim of this work is to produce high octane aromatics such as toluene and xylenes by using prepared chromia-alumina catalysts and commercial platinum-alumina catalysts with different promoters in a fixed bed reactor with various range of temperatures and LHSV, with no added hydrogen.

EXPERIMENTAL WORK

Materials

Naphtha feedstock

Heavy naphtha with 0.7388 specific gravity and 84ppm sulfur content obtained from Al-Dura Refinery is used.The properties of this naphtha are tabulated in table (1).

Table 1 The Properties of Heavy Iraqi Petroleum naphtha

Property	Unit	Data
Specific Gravity at 5.6/15.6°C	-	0.7388
API	-	60
Distillation		
I.B.P	°C	66
10 vol.% distilled	°C	95
50 vol.% distilled	°C	122.5
90 vol.% distilled	°C	148.5
F.B.P	°C	166.5
Total distillate	vol.%	98.5
Total recovery	vol.%	99.5
Residue	vol.%	1
Loss	vol.%	0.5
Kinematic Viscosity at 40°C	m^2/s	6.767×10^{-7}
Aniline Point	°C	55
Sulfur Content	ppm	84
Mwt.	g/gmol	105
Critical Temperature	°C	287
Critical Pressure	psi	440
Total Aromatics	vol.%	5.90

Hydrogen

It was supplied from Al-Mansour plant, G.C. analysis of this gas shows that the purity is 99.9%.

Nitrogen

The nitrogen was supplied from Diglah factory, G.C. analysis of this gas shows that the purity is 99%.

Chemical compounds

Various types of chemical compounds are used. They are obtained .from various places. These chemical compounds are: Chromium trioxide (CrO_3=99.99Mr) (Hopkin and Williams Searle Company), potassium nitrate (KNO_3=101.11Mr) (Hopkin and Williams) Searle Company), Cesium nitrate ($CsNO_3$= 194.91Mr) (Fluka-Garanite).

Catalyst and support

Pt/γ-Al_2O_3(RG 412), RePt/γ-Al_2O_3 (RG 482) catalysts are obtained from Al-Dura Refinery, while SnPt/γ-Al_2O_3 catalyst is obtained from Beji Refinery. γ-Al_2O_3 spherical shape support was supplied from That Al-Sawari Company. Physical and chemical properties of these catalyst and support are given in Table (2).

Catalyst Preparation

1.KCr/γ-Al_2O_3

90g of KCr/γ-Al_2O_3 catalyst with a composition of 7wt.% of Cr_2O_3 and 1wt.% of K_2O was prepared.The deposition of the active component and promoter on the supporting material (γ-Al_2O_3) was carried out by the impregnation method.

The support (γ-Al_2O_3) was calcined at 773K for 6 hours and then keep in a desiccator to ensure removing moisture and other adsorbed materials before the impregnation step.

The impregnation solution of the active component was prepared by dissolving 100g CrO_3 in 65ml distilled water to obtain solution with 15M. The solution stirred continuously by a magnetic stirrer (LASSCO INDIA) at room temperature, until all solid particles of CrO_3 is completely dissolved. The support spherical shape particles of γ-Al_2O_3 charged to the vacuum flask of impregnation apparatus and kept under less than 5 mmHg vacuum pressure for 15 min. before the impregnation solution flow through the separating funnel and cover them. The impregnation proceeds under vacuum with continuous shaking for more than 4 hours.The impregnated alumina is dried at 383K overnight, and then calcined at 773K for 6 hours, in an electrical furnace, then introduced into a desiccator.

The deposition of the active component (chromium) on the support (γ-Al_2O_3) is made by twq impregnation for process to reach the required composition successfully. It was noted that no significant changes in the deposition of active component with single impregnation process even with increasing concentration of solution.

Potassium is the promoter. It was deposited by impregnation of Cr_2O_3/γ-Al_2O_3 using the same procedure except that the impregnation solution was made by dissolving 10.7g KNO_3 in 65ml distilled water. The impregnation was carried out for one time only. The impregnated catalyst dried and calcined at the same conditions of chromium.

The final preparing catalyst is $K_2OCr_2O_3$/γ Al_2O_3.

2.CsKCr/$\gamma$$Al_2O_3$ Catalyst

50g of CsKCr/γ Al_2O_3 catalyst with a composition 7wt.% of Cr_2O_3, 1wt.% K_2O_3, and 1wt.% Cs was prepared by impregnation.

The above prepared KCr/γ Al_2O_3 catalyst was used for the impregnation with cesium nitrate solution.The impregnation solution was made by dissolving 21g $CsNO_3$ in 40ml distilled water at 323K until all solid particles are dissolved. The KCr/γ-Al_2O_3 catalyst charged to the vacuum flask of impregnation apparatus and stay under less than 5mmHg vacuum pressure for 15min before all catalyst particles covered with the impregnation solution of cerium nitrate. The impregnation carried out at 323K and for 4hours The impregnated catalyst is dried at 383K overnight, and calcined at 773K for 6 hours in an electrical furnace. Then introduced into a desiccator.

Table 2 Physical and Chemical Properties of Commercial and Prepared Catalyst

	Commercial Alumina (γ-Al_2O_3)	Commercial Pt/γ-Al_2O_3	Commercial RePt/γ-Al_2O_3	Commercial SnPt/γ-Al_2O_3	Prepared KCr/γ-Al_2O_3	Prepared CsKCs/γ-Al_2O_3
Pt, wt%	-	0.35	0.3	0.375	-	-
Re, wt%	-	-	0.3	-	-	-
Sn, wt%	-	-	-	0.57	-	-
Cr_2O_3, wt%	-	-	-	-	7	7
K_2O, wt%	-	-	-	-	1	1
CsO, wt%	-	-	-	-	-	1
Al_2O_3, wt%	99	Balance	Balance	Balance	Balance	Balance
Form	Spherical	Extrudate	Extrudate	Spherical	Spherical	Spherical
Diameter, mm	2	1.6	1.2	0.5	2	2
Surface Area, m^2/g	110	215	220	190	110	110
Pore Volume, cm^3/g	0.29	0.57	0.6	0.82	0.29	0.29
Porosity	0.45	0.80	0.85	0.75	0.45	0.45
Bulk Density, g/cm^3	1.06	0.66	0.69	0.57	1.06	1.06
Crushing Strength, kg	18	6	6	4	20	20
Loss in Atrition, wt.%	1.60	4	4	5	1.66	1.40

Aromatization Unit

Aromatic production from heavy petroleum naphtha was done in a laboratory plant unit as shown in Figure (1).

Description of Aromatization Flow Diagram

The heavy petroleum naphtha was pumped up-flow by a dosing pump inside copper tube pass through an evaporator, where naphtha is vaporized and changed from liquid to vapor phase. The vapor of naphtha enters the reactor from the top, distributed uniformly and reacted with the catalyst charged inside the reactor. The reaction products were cooled and condensed in the two high efficiency condensers cooled by ethylene glycol as refrigerant agent. Products at various conditions were collected only after steady-state condition was obtained and products before were discarded. Figure 1 shows the details of the process equipments.

Aromatization Processing Conditions

The aromatization process was examined at different reaction temperatures, liquid hourly space velocities, and with constant pressure.

Reaction temperatures varied from (703-763K), while the liquid hourly space velocities varied from (0.2-0.5h^{-1}). No added hydrogen was applied, under atmospheric total pressure.

All types of catalysts were examined at the same processing conditions above, for aim of activity comparison, and selecting the optimum conditions for aromatics production by each of them.

RESULTS AND DISCUSSION

Catalyst Performance

Physical and chemical properties of prepared and commercial catalyst such as catalyst composition, porosity, pore volume, bulk density, crushing strength and loss in attrition are determined as shown in Table 2.

Chromia-alumina catalyst promoted with potassium and cesium gives high aromatic yield.The maximum conversion of n-heptane and n-octane are 31% and 80% respectively at 673K and 0.2h^{-1}. Chromia-alumina promoted with potassium only gives low aromatic yield compared with that promoted with cesium and potassium, and that gives an indication to the strong promotion role of cesium in chromia-alumina catalyst under aromatization processing conditions.

Prepared chromia-alumina promoted by cesium and potassium is more efficient compared with commercial platinum-alumina catalyst promoted by tin or rhenium although it has low surface area (110m^2/g) and pore volume (0.29cm^3/g).The high crushing strength and low loss in attrition indicate the high stability and stamina of this catalyst.The high activity may be due to the poisoning the acid sites by potassium and cesium.This lead to hydrocracking inhibition and dehydrocyclization reaction promotion.

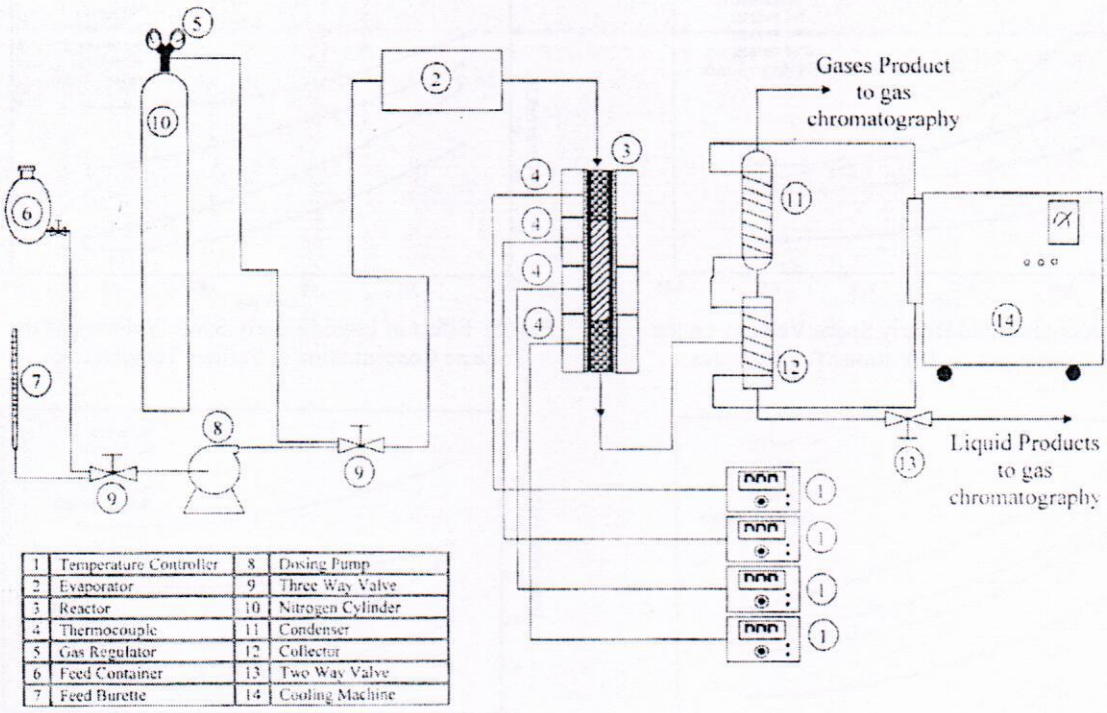

Fig. (1) Flow diagram of laboratory dehydrocyclization unit.

Effect of Temperature

The effect of temperature on aromatic yield was studied for an effective temperature range of(430-490°C) for two types of promoted chromia-alumina (KCr/γ-Al_2O_3) and (CsKCr/γ-Al_2O_3), and two types promoted platinum-alumina (RePt/γ-Al_2O_3) and (SnPt/γ-Al_2O_3) and unpromoted platinum-alumina (Pt/γ-Al_2O_3). The results of Figures (1- 10) shows that increasing in temperature results in increasing of aromatics yield.This is due to dehydrocyclization reaction of n-heptane and n-octane.

There is no significant change or increase in aromatics content at low temperatures until reaction temperature reached above 673K, when the activity of dehydrocyclization reactions increased and become dominated.In previous investigations [7, 8], the effect of temperature on the conversion of n-heptane and n-octane to toluene and xylenes respectively was studied. They found that increasing in temperature gives highly and steadily conversion with time. Also it was found that the increasing the temperature above 763K increases the cracking and consequently the rate of coke deposition.

The Effect of LHSV

The effect of LHSV on the aromatics yield was studied with an effective LHSV range for two types of promoted chromia-alumina (KCr/ γ-Al_2O_3) and (CsKCr/γ-Al_2O_3) and two types of promoted platinum-alumina (RePt/γ-Al_2O_3) and (SnPt/γ-Al_2O_3), and unpromoted platinum-alumina (Pt/γ-Al_2O_3). The results of Figures (1-10) show that decreasing in LHSV results in increasing of aromatics yield (toluene and xylenes). This is because the decreasing in LHSV of the feedstock means that increasing in the residence time, which leads to offer a plenty of contact time of the feedstock with the catalyst inside reactor, and the latter means effective conversion for n-paraffins to aromatics by increasing chances for dehydrocyclization reactions to be completed these conversions. Results indicate that low LHSV is favored for aromatization process.

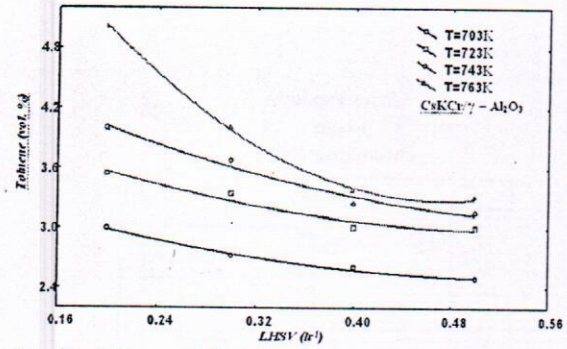

Fig. (1) Effect of Liquid Hourly Space Velocity on the Toluene Concentration at Various Temperatures.

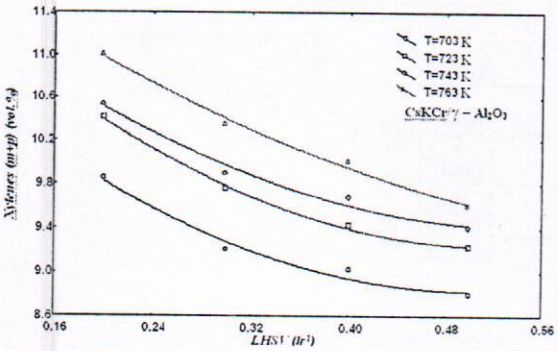

Fig.(2) Effect of Liquid Hourly Space Velocity on the Xylenes(m+p)Concentration at Various Temperatures.

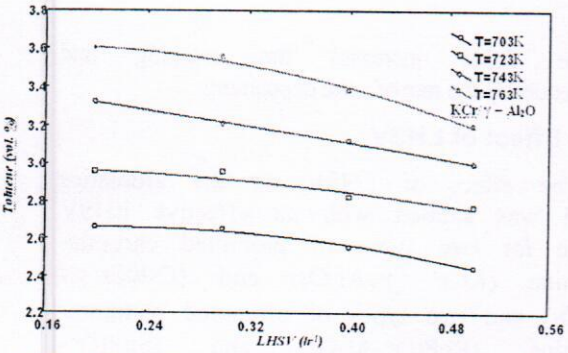

Fig.(3) Effect of Liquid Hourly Space Velocity on the Toluene Concentration at Various Temperatures.

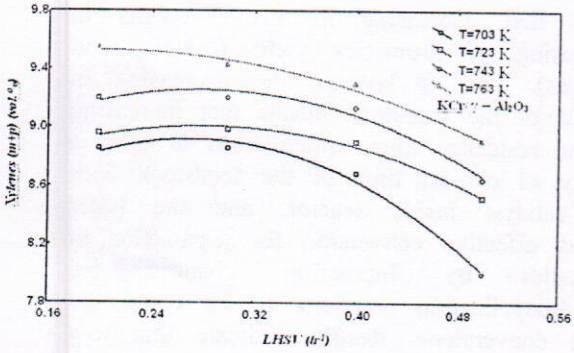

Fig.(4) Effect of Liquid Hourly Space Velocity on the Xylenes(m+p)Concentration at Various Temperatures.

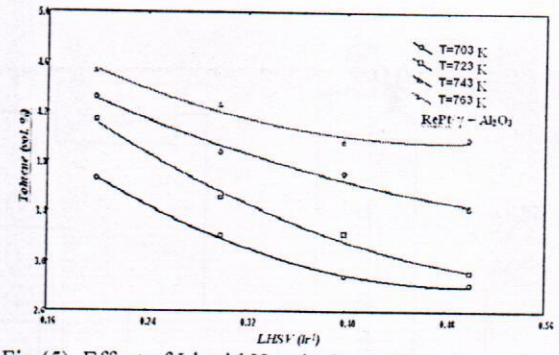

Fig.(5) Effect of Liquid Hourly Space Velocity on the Toluene Concentration at Various Temperatures.

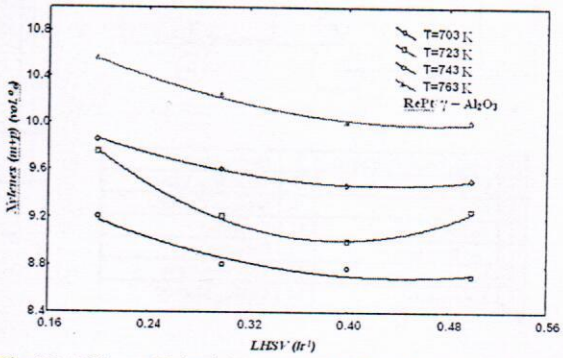

Fig.(6) Effect of Liquid Hourly Space Velocity on the Xylenes(m+p)Concentration at Various Temperatures.

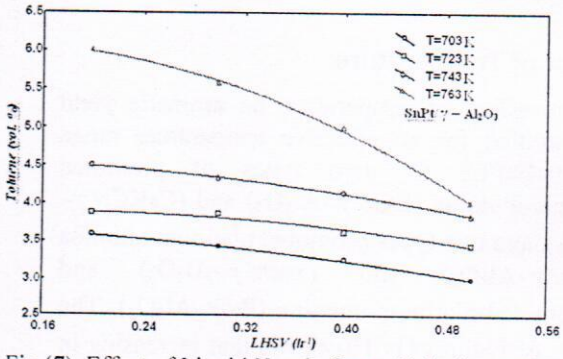

Fig.(7) Effect of Liquid Hourly Space Velocity on the Toluene Concentration at Various Temperatures.

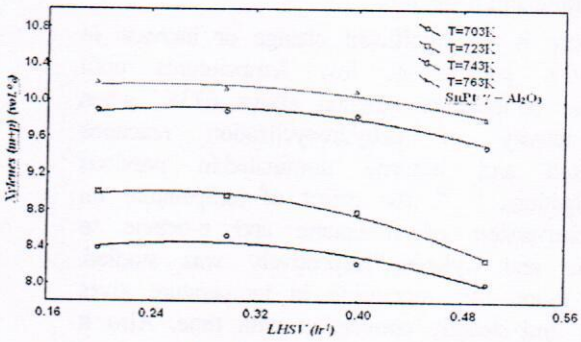

Fig.(8) Effect of Liquid Hourly Space Velocity on the Xylenes(m+p)Concentration at Various Temperatures.

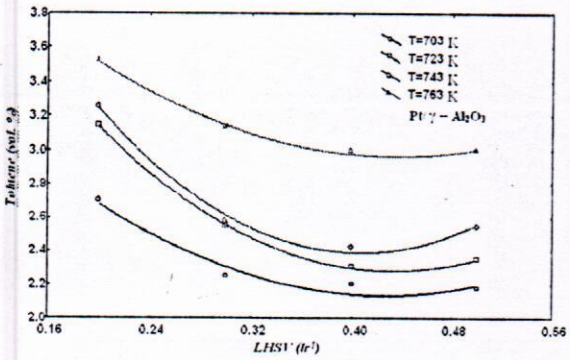

Fig.(9) Effect of Liquid Hourly Space Velocity on the Toluene Concentration at Various Temperatures.

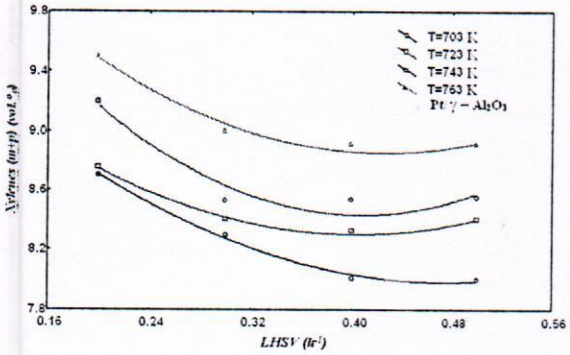

Fig.(10) Effect of Liquid Hourly Space Velocity on the Xylenes(m+p)Concentration at Various Temperatures.

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