HYDROCRACKED ATHABASCA BITUMEN AS A POTENTIAL SOURCE OF BENZENE, TOLUENE AND XYLENE

by

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INTRODUCTION

Benzene, toluene and xylene, often referred to as BTX, are much in demand as raw materials for the chemical industries[1]. They are also valuable components in gasolines because of their high octane numbers. In this report only the naphtha fractions (distilling to 205°C) produced during hydrocracking of the Athabasca bitumen are discussed. Included in the measurement of BTX potential are those cycloparaffins that might be converted to the desired compound by aromatization during platforming (reforming, powerforming, etc.[2]). The yield of naphtha, and hence BTX, could be increased by further processing of the distillate which boils above 200°C. For example, hydroprocessing of gas oils to meet sulphur and nitrogen specifications results in some naphtha formation, as does catalytic cracking. A discussion of BTX potential of naphtha produced by this further processing is beyond the scope of this paper.

EXPERIMENTAL

Samples for analysis were distilled from the product from a one barrel per day hydrocracking pilot plant using the ASTM D86 distillation[3]. Operation of the pilot plant under conditions to produce these samples has been described earlier[4,5,6]. The 4.5 ℓ reactor, which had an internal diameter of 3.81 cm, was operated using bottom feed. Reactor conditions and a partial listing of product data are given in Table 1.

All runs except run 5 were carried out in the "thermal" mode without catalyst[4,6]. In run 5 a slurry type cobalt-molybdenum-aluminum catalyst on a bituminous coal base was used. In all runs the feed flowrate was 9 ℓ/h to give a liquid hourly space velocity (LHSV) of 2.0. Pitch conversion is defined as disappearance of material boiling above 524°C equivalent atmospheric boiling temperature. The naphtha fraction of the product was determined using a standard method[3], and FIA results were determined on the naphtha

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(1) Oilweek, June 21/76, p 12

2. Text book

TABLE 1

Hydrocracking Reaction Conditions and Product Data

Sample from Run Number		4	5	3	2	1
LHSV		2.0	2.0	2.0	2.0	2.0
Pressure	MPa	24.2	13.89	13.89	13.89	13.89
Temperature	^{o}C	470	460	460	430	410
Catalyst		Nil	Coal/ CoMo	Nil	Nil	Nil
Pitch Conversion	wt %	89.1	82.5	79	49.3	26.1
Naphtha Fraction		17.4	10.4	9.0	12.5	14.6
FIA results of Naphtha						
Saturates		61.0	67.4	56.5	49.8	48.5
Olefins		30.5	22.1	34.5	37.7	36.4
Aromatics		8.5	10.4	9.0	12.3	14.6
% S of Gasoline		0.87	0.32	0.84	1.57	1.80

DISCUSSION

In Table 2, the amounts of benzene, toluene and xylene of the various samples of the gasoline samples are shown. Ethyl benzene has been included because it is a precursor for styrene. Considerable amounts of benzene are consumed commercially in the manufacture of ethyl benzene. Table 2 is difficult to interpret as is, and should be considered along with the analyses in Table 1. An increase in severity of hydrocracking, as shown in Table 1 by the increases in temperature and pressure in runs 1-4, results in an increase in the volume of naphtha, and a decrease in the amount of aromatics in this naphtha. This is also shown in Table 3 which gives BTX and ethyl benzene as a percentage of the whole product. It shows that the amounts of these chemicals available, as a percentage of the total product, increases with hydrocracking severity.

Table 3 also shows that catalytic hydrocracking (run 5) produced about 20% more BTX than thermal (run 3) for an equivalent pitch conversion and reactor pressure.

If it was desired to produce BTX from a naphtha stream, this stream would almost certainly be catalytically reformed. Tables 4 and 5 give possible BTX and ethyl benzene precursors on a sample and whole product basis, respectively.

The amounts of possible precursors of the desired aromatic compounds are shown in Table 4.

The actual amounts in the whole hydrocracked bitumen samples are shown in Table 5.

The C_6 naphthenes which comprise the first three compounds in Table 5, and which are possible precursors of benzene, total 0.11%, 0.55%, 0.75%, 0.92% and 0.56% for the samples. When these values are added to the benzene values, the amounts of possible benzene are 0.15%, 0.68%, 0.89%, 1.07% and 0.70% for the samples.

The possible precursors of toluene (C_7 naphthenes) total 0.05%, 0.23%, 0.49%, 0.75% and 0.39%. Added with the toluene values, the possible amounts of toluene would be 0.10%, 0.43%, 0.73%, 1.04% and 0.67% for the five samples. The amounts of C_8 naphthenes are 0.14%, 0.33%, 0.38%, 0.50% and 0.25%. Therefore, the total amounts of xylenes and ethylbenzene would be 0.22%, 0.46%, 0.52%, 0.11% and 0.44%.

TABLE 2

Amounts of Benzene, Toluene, Xylene and Ethylbenzene in Naphtha Fractions

Sample		4	5	3	2	1
Benzene	%	0.85	1.25	1.03	1.23	0.92
Toluene		1.68	2.41	1.84	1.90	1.22
Xylene		0.85	1.26	0.67	0.93	1.20
Ethyl-benzene		0.34	0.47	0.36	0.24	0.71
Total (BTX)		3.38	4.92	3.54	4.06	3.34

TABLE 3

Amounts of Benzene, Xylene, Toluene and Ethyl Benzene In the Whole Hydrocracking Sample

Sample		4	5	3	2	1
Benzene	%	0.15	0.14	0.14	0.13	0.04
Toluene		0.29	0.28	0.24	0.20	0.05
Xylene		0.15	0.14	0.09	0.10	0.05
Ethyl-benzene		0.06	0.05	0.05	0.03	0.03
Total (BTX)		.59	.56	.47	.43	.15

TABLE 4

Amounts of Possible Precursors of Desired Aromatic Compounds in the Naphtha Fractions of Hydrocracked Athabasca Bitumen Samples

	1	2	3	4	5
1-methyl-1-cyclopentene	1.21	2.04	2.24	2.28	1.83
methylcyclopentane	0.56	1.05	1.02	0.73	0.76
cyclohexane	1.15	2.19	2.39	2.24	2.26
1,3-dimethylcyclopentane	0.40	0.90	1.34	1.11	0.90
methylcyclohexane	0.38	0.32	1.08	1.87	1.36
ethylcyclopentane	0.59	0.99	1.25	1.32	1.15
{1-methyl-cis-3-ethylcyclopentane 1-methyl-1-ethylcyclopentane}	0.75*	0.70*	0.50*	0.72*	0.60*
1,3- + 1,4-dimethylcyclohexane	1.35	1.15	0.99	1.03	0.07
1-cis-2-dimethylcyclohexane	1.39	1.33	1.37	1.12	1.50
Total	7.78	10.67	12.18	12.42	10.43

* Estimates

TABLE 5

Amounts of Possible Precursors of Desired
Aromatic Compounds in Whole Hydrocracked Bitumen Samples

	1	2	3	4	5
1-methylcyclopentane	0.05	0.21	0.30	0.40	0.21
methylcyclopentane	0.02	0.11	0.13	0.13	0.09
cyclohexane	0.04	0.23	0.32	0.39	0.26
1,3-dimethylcyclopentane	0.02	0.10	0.18	0.19	0.16
methylcyclohexane	0.01	0.03	0.14	0.33	0.16
ethylcyclopentane	0.02	0.10	0.17	0.23	0.13
methylethylcyclopentane	0.03	0.07	0.07	0.13	0.07
dimethylcyclohexane	0.11	0.26	0.31	0.37	0.18
Total	0.30	1.11	1.62	2.17	1.20