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Dehydrocyclodimerization

II. Dehydrocyclodimerization of Propane and Pentane over Supported Platinum Catalyst

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The principal aromatic produced in the dehydrocyclodimerization of propane is benzene. Pentane gives more high molecular weight products, such as naphthalenes and other condensed aromatics. Ultimate recycle yields and conversions to aromatics increase with increasing carbon number of the reactant light paraffin.

Dehydrocyclodimerization converts light paraffins to aromatics. In the first part of this series, we have shown the reactions of butanes (*1*). Here we discuss the behavior of propane and pentane. Reaction conditions and analytical techniques were the same as those used with the butanes. The catalyst was 0.8% Pt on alumina.

Hydrocarbons used were: Propane (Matheson, C. P.) 99.91% pure, containing 0.005% 1-butene, 0.055% *n*-butane, and 0.023% ethane,* and *n*-pentane (Phillips, pure grade) 99.78% pure, containing 0.034% isopentane, 0.004% cyclopentane, 0.13% pentenes, and 0.05% other hydrocarbons.*

Product compositions at two space velocities are shown for propane in Table 1. Conversions to aromatics are lower than those obtained from the butanes. Benzene and toluene are the predominant aromatics formed. C_4 hydrocarbons and small amounts of pentenes are also formed. Experiments at different catalyst onstream times show a slower catalyst deactivation for propane than for the butanes.

The results for *n*-pentane given in Table 2 show that pentane conversions to aromatics are higher than those of the butanes (*1*). Xylenes and ethylbenzene are formed at their equilibrium concentrations. Aromatics from *n*-pentane and isobutane are different in that a substantial amount of the aromatics from *n*-pentane is naphthalenes (Table 3). The distribution according to carbon number of the aromatics has three maxima (Fig. 1). The first maximum

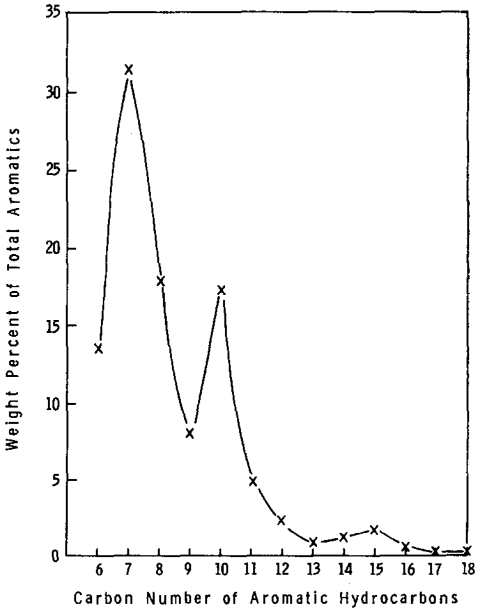

FIG. 1. Distribution according to carbon number of aromatic hydrocarbons produced by dehydrocyclodimerization of *n*-pentane over Pt-alumina catalyst at 560°C with a LHSV of 1.1.

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* Gas chromatographic analysis.

TABLE 1

DEHYDROCYCLODIMERIZATION OF PROPANE OVER 0.8% PLATINUM ON ALUMINA CATALYST AT 560°C TEMPERATURE AND 1 atm TOTAL PRESSURE

Liquid hourly space velocity:	2.1	0.84
Product composition (wt %)[a]		
Unreacted propane	45.58	21.41
Propylene	16.05	9.07
Butanes	0.39	0.24
Butenes	0.79	0.40
Butadiene	0.04	0.02
Pentenes	0.05	0.23
Benzene	4.19	7.26
Toluene	1.69	3.41
Ethylbenzene	0.22	0.23
m- and *p*-Xylenes	1.11	1.48
o-Xylene	0.50	0.65
Styrene	0.19	0.21
1-Methyl-3-, and 4-Ethylbenzenes	0.31	0.98
1,2,4-Trimethylbenzene	0.43	
Indan and other C_9 aromatics		
Indene	0.20	0.48
Methane	9.98	22.02
Ethane, ethylene	14.64	
Acetylene	0.01	
Coke[b]	2.29	7.43
Hydrogen	1.34	1.19
Total	100.00	100.00
Total aromatics	8.84	14.70
Yield (wt %)[c]	24	21
Isobutylene/*n*-butenes	0.75	0.77

[a] At reaction effluent sampling times of 12–14 min.

[b] Coke was calculated from the carbon content of the used catalyst.

[c] Ultimate yields were calculated assuming that all C_3–C_4–C_5 hydrocarbons are recycled.

TABLE 2

DEHYDROCYCLODIMERIZATION OF *n*-PENTANE AT 560°C TEMPERATURE AND AT 1 atm PRESSURE OVER 0.8% PLATINUM-ON-ALUMINA CATALYST

Liquid hourly space velocity:	1.1	2.6
Reaction effluent sampling time (Min):	15	8
Product composition (wt %)		
Unreacted *n*-pentane	5.29	5.99
Isopentane	2.27	2.63
Pentenes	4.05	5.07
1,3-Pentadienes	0.21	0.29
Isoprene	0.12	0.17
Cyclopentane	0.20	0.26
Cyclopentene	0.21	0.42
Cyclopentadiene	0.74	0.84
C_6–C_7 Alkylnaphthenes	1.73	
Benzene	4.60	5.75
Toluene	8.96	8.66
Ethylbenzene	0.58	0.72
m- and *p*-Xylenes	3.13	3.00
o-Xylene	1.41	1.50
Styrene	0.22	0.28
Methylethylbenzenes	0.93	0.96
1,2,4-Trimethylbenzene	1.43	1.24
Indan	0.44	0.40
Indene	1.03	1.16
C_{10} Alkylbenzenes	0.98	1.15
Methylindenes	0.72	1.27
Naphthalene	7.77	9.34
Methylnaphthalenes	2.30	1.96
Methane	9.92	11.97
Ethane, ethylene	10.27	9.70
Propane, propylene	11.83	12.83
Isobutane	0.92	0.69
n-Butane	2.77	2.05
Butenes	3.45	2.66
Butadiene	0.07	0.07
Coke	7.80	3.64
Hydrogen	3.65	3.34
Total	100.00	100.00
Total aromatics	34.50	37.38
Yield (wt %)[a]	52	56.5
Iso/normal ratio: pentenes	1.7	2.0
Iso/normal ratio: pentadienes	0.6	0.6
Iso/normal ratio: butenes	0.6	

[a] Ultimate yields were calculated assuming that all C_3–C_4–C_5 hydrocarbons are recycled.

is at seven carbon atoms, and the other two maxima are at 10 and 15. The maximum at 10 carbon atoms is higher at shorter contact times. Dimers and trimers (hydrocarbons with 10 and 15 carbons) are the primary products of pentane dehydrocyclodimerization. Other aromatics may be formed by the dealkylation of these primary products, by dehydrocyclodimerization of cracked products, or by transalkylation of aromatic products (i.e., disproportionation).

TABLE 3
Aromatic Ring System Distribution—Comparison of Isobutane and *n*-Pentane[a]

Hydrocarbon:	Isobutane	*n*-Pentane
Ring systems present (wt %) of total aromatics produced[b]		
Alkylbenzenes	93.7	73.5
Naphthalenes	4.6	17.7
Indanes	0.3	1.6
Indenes	1.2	3.1
Fluorenes	0.11	1.5
Anthracenes, phenanthrenes	0.09	2.2
Pyrene		0.35
Benzanthracene		0.05

[a] Over 0.8% platinum-on-alumina catalyst, at 560°C, with an LHSV of 1.

[b] Based on liquid product analyses.

As with the butanes, iso/normal ratios of the butenes and pentenes made from pentane are near equilibrium. Note also the formation of cyclopentane, cyclopentene, and cyclopentadiene (Table 2).

We may conclude from comparing propane, butane, and pentane results that recycle yields and conversions to aromatics increase with increasing carbon number of the feed hydrocarbon.

REFERENCE

1. Csicsery, S. M., *J. Catal.* **17**, 207 (1970).