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Batch Hydrogenolysis Reactions of Pure Compounds Related to Petroleum Oils

Most studies of high pressure hydrogenation of fossil fuels have been directed toward production of premium liquid fuels, in the presence of catalyst at temperatures low enough to avoid appreciable gas formation (*14*). Some work was done with pure organic compounds in an effort to locate temperatures at which rapid dissociation into fixed gases begins (*3, 7, 10*). The batch system work of Kling and Florentin (*3*) showed that at sufficiently high initial hydrogen pressures, appreciable gasification was initiated in the absence of catalyst at 410° to 440° C. (770° to 824° F.) for paraffins of higher molecular weight, at 440° C. (824° F.) for anthracene, and at 475° C. (887° F.) for naphthalene. These data, supported by others for polynuclear aromatics (*2, 13*), showed that fossil fuels could be converted to gas without catalyst by raising operating temperatures above the limits prescribed for high yields of liquid products.

In view of the increased importance of pipeline natural gas as an energy source, and attendant problems of peak-load gas supply, pyrolysis of liquid fossil fuels in the presence of hydrogen (hydrogasification) has been investigated as part of a continuing program concerned with production of natural gas supplements and substitutes near the point of consumption (*4, 5, 9, 12*). Conventional methods, which do not employ superatmospheric pressure or an outside source of hydrogen, produce substantial quantities of liquid by-products and coke, but relatively little gas of high olefin content.

High pressure hydrogenolysis (destructive hydrogenation with rapid formation of C_1-C_3 hydrocarbons) at 1200° to 1350° F. (649° to 732° C.) was studied as an extension of research on lower pressure (up to 60 pounds per square inch gage) hydrogasification of petroleum oils and natural gas liquids, to increase conversion to methane and to explore operating conditions for gasification of residual oils of high molecular weight and low hydrogen content. Batch reactor tests indicated that at 1200° to 1350° F., 2000 to 4400 pounds per square inch gage, and suitable hydrogen–oil feed ratios, distillate and residual petroleum oils could be converted at high rates to gases containing over 90 mole % methane, and to only small amounts of nongaseous product (*12*). Vapor phase reaction to gaseous products was rapid after attainment of a characteristic threshold temperature in the range reported by Kling and Florentin (*3*).

The thermal hydrogenolysis of several pure hydrocarbons related to petroleum oils has been studied with a similar technique.

Apparatus and Procedure

The high-temperature, high-pressure reactor, constructed from 19-9DL alloy, was 2 inches in inside diameter, $4^3/_8$ inches in outside diameter, and 20 inches in inside length. The system volume was 1006.9 ml. The Autoclave Engineers self-sealing closure (*1*) was adapted for high-temperature service by the use of boundary lubricant, molybdenum disulfide, on the outside surface of the seal ring. A thin, even layer applied as an aerosol (Moly-Spray-Kote, Alpha Corp.) completely prevented seizure marks ordinarily arising above about 1000° F. because of the similarity of the 19-9DL alloy body and the 16-25-6 alloy seal ring. The oxidation products of molybdenum disulfide are abrasive, but the rate of oxidation was too slow to form appreciable amounts of oxides, and those formed were confined to the seal ring surface above the area of sealing contact. Tests with graphite prepared as an aerosol (Spray/Graph, American Resin Corp.) indicated that a continuous layer could not always be maintained at high temperatures. Occasional minute seizure marks were noted, although operation was greatly improved, and feasible if a little wear could be tolerated.

A thermocouple well, $^3/_8$ inch in outside diameter, extended concentrically for 15 inches into the reaction space of the vessel. The reactor temperatures reported are maximum; they were sensed 14.5 inches from the top of the reaction space by a fast-response Chromel-Alumel thermocouple and measured by a portable potentiometer equipped with an ice-water reference. Little variation in axial temperature for about 18 inches of the 20-inch inside reactor length was noted; chilling of the reactor contents by closure and bottom surfaces was confined to a layer of 1 inch or less at the top and bottom. Average reactor temperatures (in degrees absolute) were estimated about 1% lower at 1200° F. and 1.5% lower at 1300° F. than maximum temperatures used in calculations.

Pressures were measured with a Heise Bourdon tube gage 10 inches in diameter, calibrated against a dead weight gage. Reactor pressure was indicated continuously, except that in the run with naphthalene it was measured only at time of sampling of gaseous products.

Feed hydrogen was a commercial grade (National Cylinder Gas Co.) analyzing over 99.9% pure by mass spectrometer. The reactor was charged at room temperature, and placed in the rocking furnace, which was also at room temperature. Heating at full input (4.5 kw.) was maintained throughout the rising temperature portion of every run, temperature rising 8° to 10° F. per minute. Some runs were terminated before the attainment of 1300° F.; others were continued at 1300° F. for a time. In all cases reaction was initiated below 1300° F., and most attention was given to the rising temperature portion of each run.

Sources and Purities of Hydrocarbons Tested

n-Hexane. Phillips Petroleum Co., pure grade, 99 mole % min.
n-Octane. Distillation Products Industries, P1107, b.p. 124–6° C.
n-Decane. Matheson Co., 5845, b.p. 173–5° C.
n-Dodecane. Matheson Co., 5830, b.p. 111–14° C./30 mm.
Cyclohexane. Matheson Co., 2825, b.p. 80–1° C.
Cyclohexane. Phillips Petroleum Co., pure grade, 99 mole % min.
Benzene. Matheson Co., CB-209, reagent grade ACS, b.p. 79.5–81° C.
Decahydronaphthalene (Decalin). Matheson Co., P2854, b.p. 190–3° C.
1,2,3,4-Tetrahydronaphthalene (Tetralin). Distillation Products Industries, P550, b.p. 205–7° C.
Naphthalene. Matheson Co., 2616, recryst. from alc., m.p. 79–80° C.
Ethane. Matheson Co., 95.0% purity; analysis by mass spec., 93.0% C_2H_6, 3.5% C_2H_4, 0.9% C_3H_6, 0.2% 1,3-butadiene, 0.7% H_2, 1.7% N_2 + CO

Table I. Batch Hydrogenolysis of *n*-Paraffin Hydrocarbons and

	Run 134 *n*-Hexane, 0.1016 lb.								Run 93 *n*-Octane, 0.0999 lb.				Run 101 *n*-Decane, 0.0998 lb.			
Initial conditions																
Pressure, lb./sq. inch gage	1275								1275				1275			
Temperature, ° F.	73								80				81			
Hydrogen, lb.-mole	0.007106								0.007056				0.007063			
Hydrocarbon, lb.-mole	0.001179								0.000875				0.000701			
Threshold temp., ° F.	860[a]								797[b]				905[b]			
Gas sample designation	A	B	C	D	E	F	G	H	A	B	C	D	A	B	C	D
Residence time above room temp., min.	80	88	99	111	124	135	151	169	75	93	115	132	89	97	106	120.5
Pressure, lb./sq. inch gage	3330	3530	3700	3880	4050	4170	4115	4090	3145	3535	3860	4095	3440	3530	3645	3835
Temperature, ° F.	863	940	1042	1140	1230	1299	1299	1303	825	1003	1177	1298	968	1039	1110	1213
Total reaction mass, lb.-mole × 10^3	8.376	8.389	8.194	8.065	7.969	7.882	7.779	7.714	8.147	8.039	7.842	7.745	8.014	7.835	7.723	7.623
Recovered components[d], moles/mole feed																
$N_2 + CO + CO_2$	0.018	0.018	0.025	0.026	0.019	0.019	0.025	0.019	0.009	0.027	0.070	0.018	0.040	0.061	0.054	0.064
H_2	5.84	5.73	4.87	3.74	3.48	2.94	2.25	2.05	8.13	7.71	4.78	3.53	9.38	7.91	5.67	4.97
CH_4	0.006	0.042	0.432	1.28	1.55	2.51	3.67	3.97	...	0.103	1.99	3.71	0.109	0.758	2.26	2.97
C_2H_6	0.006	0.084	0.508	1.32	1.29	0.821	0.280	0.136	...	0.120	1.70	1.24	0.169	0.809	2.28	2.51
C_3H_8	...	0.084	0.425	0.045	...	...	...	...	...	0.052	0.009	...	0.109	0.563	0.375	...
C_4H_{10}	...	0.012	0.019	...	...	...	...	...	0.018	0.017	0.009	...	0.030	0.092	0.032	0.032
C_5H_{12}	...	...	...	...	...	...	...	...	...	0.026	0.009	...	0.020	0.020	0.011	...
C_6H_{14}	0.041	0.036	0.044	...	...	...	...	...	0.027	0.043	0.026	0.009	0.050	...	...	...
C_8H_{18}	...	...	...	...	...	...	...	...	0.657	0.464	0.122	0.088	...	...	...	...
C_2H_4	...	0.006	0.019	0.039	0.038	0.019	0.006	...	...	...	...	...	...	...	...	...
C_3H_6	...	0.012	...	...	...	...	...	...	...	...	...	...	...	...	...	...
C_4H_8	...	...	...	...	...	...	...	...	...	...	...	0.220	...	...	...	...
C_5H_{10}	...	...	...	...	...	...	...	...	0.018	0.017	...	...	0.020	0.020	0.021	0.021
C_6H_{12}	...	...	...	...	...	...	...	...	0.018	0.017	...	...	0.010	0.010	0.011	0.011
C_7H_{14}	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Butadiene	...	0.006	0.006	...	...	...	...	...	...	...	...	...	...	...	...	...
Benzene	...	...	...	...	...	0.006	...	...	0.009	...	...	...	...	...	...	...
Toluene	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Ethylbenzene	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Total C_4+ components[d,f], moles/mole feed	1.24	1.16	0.671	0.393	0.433	0.378	0.369	0.369	1.17	1.18	0.422	0.346	1.63	1.08	0.371	0.361
Conversion to C_1-C_3 paraffins[d,g], %	0.25	7.7	45.4	67.5	68.8	69.2	70.5	70.7	0	6.3	67.5	77.5	7.7	40.7	78.5	79.9

[a] Estimated by extrapolation of conversion data. [b] Determined at break in temperature-time curve. [c] Determined from pressure maximum data. [d] Calculated from total number of moles of reaction mass and from carbon balance based upon composition of recovered components, assuming carbon number of

Samples were taken at intervals by bleeding the sample into an evacuated 10-ml. bottle without passage through absorbers or condensers. The volume of purge and sample gas for three to seven samplings was usually less than 0.5% of the reaction mass volume. Analyses were made with a Consolidated Engineering Co. Model 21-103 mass spectrometer. Above 800° F. total moles of reaction mass were calculated by the ideal gas law from observed pressure and temperature, and at room temperature by application of compressibility data. Some unpublished compressibility data for the ethane-hydrogen system developed in the institute's laboratories were utilized. The full reactor volume at high temperatures, and the free volume (reactor volume less sample volume) at room temperature, were used in the calculations.

Presentation of Results

Major products of thermal hydrogenolysis were gaseous paraffin hydrocarbons of lower molecular weight. Gaseous products heavier than ethane were almost completely converted to ethane and methane below 1300° F.; slow hydrogenolysis of ethane at 1300° F. yielded methane as the ultimate stable product.

Higher molecular weight components of the reaction mass were incompletely recovered because of condensation in the high pressure portion of the sampling system. Recovered and unrecovered components were estimated from the total moles of the reaction mass, carbon balance based on mass spectrometer analysis, and an assumed average carbon number of the unrecovered components. For all feedstocks, except benzene, Tetralin, and naphthalene, estimates were made by averaging two values calculated on the basis that the unrecovered components consist (1) only of C_4 hydrocarbons and (2) only of hydrocarbons with the same carbon number as the feed. This assumes that all C_3 and lower molecular weight components were recovered by sampling and that no components with a higher carbon number than the feed were formed. Because components with carbon numbers between three and those of the feed appeared negligible in benzene, Tetralin, and naphthalene runs, reported results are based on the assumption that unrecovered material consisted only of C_6 or C_{10} hydrocarbons.

The uncertainty in estimated values of recovered components introduced by assuming a range of possible carbon numbers of the unrecovered components is normally less than 3%. The average uncertainty for unrecovered component is, however, on the order of 30% because of their relatively low abundance; the uncertainty in the total C_4^+ components (recovered and unrecovered) shown in Figures 1 and 2 and Tables I and II is somewhat reduced by including yields of recovered C_4^+ components known with considerable certainty.

The true values for the total C_4^+ components up to the start of rapid gasification would be closer to those based on a carbon number of unrecovered material equal to that of the feed. Thus, the high reported C_4^+ values (more than 1 mole per mole of feed) at reactor temperatures below 1100° F. are probably in part the result of using constant average carbon numbers for the unrecovered components over the entire run period. As significant quantities of hydrocarbons other than original feed and/or its primary cracking, dehydrogenation, and cyclization products would probably not persist as a reactor temperature of 1300° F. is approached, the reported final C_4^+ values may also be high. No significant formation of carbon or high molecular weight residues was noted except with naphthalene; this indicates that the assumption of a maximum carbon number for the unrecovered components equal to that of the feed is sound.

Cyclic C_{10}-Hydrocarbons

Run 90 n-Dodecane, 0.0989 lb.				Run 97 Decalin, 0.0995 lb.				Run 117 Tetralin, 0.1014 lb.			Run 133 Naphthalene, 0.1000 lb.						
1275				1275				1270			1275						
80				80				83			70						
0.007093				0.007151				0.007116			0.007375						
0.000580				0.000720				0.000761			0.000780						
964^{b}				918^{b} and 1000^{c}				1006^{b} and 1150^{c}			1020^{b} and 1050^{c}						
A	B	C	D	A	B	C	D	B	C	D	A	B	C	D	E	F	G
91	97	116	131	81	89	99	125	122.5	137	153	93	104	115	132.5	139	148	159
3445	3540	3790	3990	3255	3365	3170	3405	3430	3015	2865	3470	3540	3250	2410	2330	2300	2260
975	1033	1188	1285	918	978	1080	1255	1183	1274	1295	951	1049	1137	1265	1300	1295	1303
7.988	7.889	7.649	7.604	7.862	7.787	6.852	6.607	6.947	5.789	5.437	8.183	7.805	6.773	4.657	4.414	4.370	4.295
0.125	0.127	0.051	0.064	0.046^{e}	0.046^{e}	0.033^{e}	0.062^{e}	0.128^{e}	0.113^{e}	0.104^{e}	0.028^{e}	0.018^{e}	0.032^{e}	0.033^{e}	0.031^{e}	0.021^{e}	0.020^{e}
10.4	9.60	6.39	5.26	9.12	8.96	7.21	2.75	6.40	3.17	0.459	9.46	8.97	7.00	1.76	0.633	0.425	0.440
0.149	0.835	3.21	5.16	...	0.027	0.331	4.27	0.912	2.62	5.89	...	0.009	0.323	2.68	4.01	4.51	4.44
0.263	1.01	3.00	2.22	...	0.018	0.232	1.69	0.870	0.942	0.195	...	0.009	0.347	0.896	0.398	0.077	0.030
0.183	0.860	0.013	...	...	0.027	0.190	0.009	0.017	0.007	0.007	...	...	0.032	0.005	0.005	...	0.005
0.091	0.139	...	...	...	0.009	0.042	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	0.041	0.009	...	...	...	...	...	...	...	...	...	...
0.057	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
...	...	0.051	...	...	...	...	...	...	0.014	...	...	...	0.008	0.016	0.010	...	...
...	0.013	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
...	...	...	0.025	...	0.009	...	...	...	...	...	...	...	...	...	...	...	...
0.057	0.025	...	...	...	0.018	0.050	0.018	...	...	...	...	...	...	...	...	...	...
0.023	0.013	...	...	0.065	0.018	0.058	0.018	...	...	...	...	...	...	...	...	...	...
...	0.013	...	...	...	...	0.091	0.027	...	...	...	...	...	...	...	...	...	...
...	...	...	...	...	0.009	...	...	...	...	...	...	...	...	...	...	...	...
0.023	0.013	0.013	0.013	...	...	...	0.053	0.171	0.205	0.272	...	...	0.110	0.066	0.131	0.077	0.050
...	...	...	...	...	...	...	0.009	0.017	0.007	0.035	...	...	0.024	...	0.016	0.015	0.010
...	...	...	...	...	...	...	...	0.017	0.007	...	...	...	0.008	...	...	...	...
1.83	1.16	0.452	0.414	1.75	1.74	1.53	0.396	0.807	0.741	0.490	1.00	1.00	0.941	0.575	0.574	0.569	0.572
10.9	45.3	77.1	80.0	0	1.5	13.6	76.8	27.1	45.3	62.9	0	0.26	11.2	44.9	48.2	46.7	45.1

unrecovered components to range from four to that of feed for n-paraffins and Decalin, to and equal ten for Tetralin and naphthalene. ^{e} N_2 + CO_2. ^{f} Includes unrecovered C_4+ components. ^{g} By carbon balance.

Threshold Behavior

Batch reactor tests indicate the nature of the primary reactions through plots of the type shown in Figure 3. For nearly constant initial conditions—0.070 to 0.074 pound-mole of hydrogen per pound of hydrocarbon and 1275 pounds per square inch gage—the temperature-pressure relationship in the absence of chemical reaction, assuming ideal gas behavior, would be approximately linear, with some curvature due to the gradual vaporization of feed. Final pressures would vary from 4000 to 4500 pounds per square inch gage at 1300° F., for the hydrocarbons studied. The hydrogen-hydrocarbon systems showed the following characteristics at a nearly constant heat-up rate of 8° to 10° F. per minute.

For paraffins, the rate of pressure rise was approximately constant up to 1300° F. and reached a level of about 4000 pounds per square inch gage, as anticipated from an equimolar paraffin hydrogenolysis system such as $C_nH_{2n+2} + H_2 \rightarrow C_mH_{2m+2} + C_{(n-m)}H_{2(n-m)+2}$. Rapid formation of C_1-C_3 hydrocarbons began at approximately 900° F. With paraffins of higher molecular weight, the temperature-time curve broke sharply as initial gasification temperature was approached.

For saturated or partially saturated cyclic hydrocarbons, the reactor pressure passed through a well-defined maximum at 900° to 1000° F., followed by rapid C_1-C_3 hydrocarbon formation. The occurrence of pressure maxima before initiation of rapid gas formation indicates that primary hydrogenation or hydrocracking reactions of the feed hydrocarbons, such as formation of cyclohexane from cyclohexene, may precede hydrogenolysis (note double pressure maximum for cyclohexene in Figure 3). Pressure levels during gasification were substantially below those observed with n-paraffin feeds because of the lower hydrogen content of the reaction systems. For cyclic hydrocarbons of higher molecular weight, a threshold temperature determined by a sharp break in the temperature-time curve was again observed as the initial gasification temperature was approached.

For benzene and naphthalene, initial gasification temperatures were relatively high, 1150° and 1050° F., as anticipated for these thermally stable aromatics. The pressure drop after initiation of C_1-C_3 paraffin formation was very steep, because of the large decrease in total moles typical of hydrogenolysis reactions of highly unsaturated feeds.

The breaks in the temperature-time curves with the hydrocarbons of higher molecular weight (Figure 3) could be due to rapid feed vaporization or initiation of primary endothermic reactions. Although the absence of a temperature break for the more volatile feeds of low molecular weight appears to support the vaporization concept, this explanation must be rejected because the observed threshold temperatures are 140° to 250° F. higher than the pure feed hydrocarbon critical temperatures. The threshold phenomenon is probably due to primary endothermic thermal cracking reactions, which may immediately precede exothermic hydrocracking, hydrogenation, or hydrogenolysis. Similar breaks were observed by Pearce and Newsome (*8*) at 490° C. (914° F.) at 15,000 pounds per square inch.

Occurrence of pressure maxima and initiation of rapid gas formation must be related to reaction of the feed hydrocarbon, or its primary products, with hydrogen. Insufficient analytical data were obtained to define more closely the possible primary reactions of the feed hydrocarbon: thermal cracking, hydrogenation, and hydrocracking (destructive hydrogenation with negligible gas formation).

Hydrogenolysis Behavior

The initial stages of gasification were characterized by nearly equimolar production of methane and ethane. Initial propane formation varied widely with feed hydrocarbon composition; approximately equimolar formation occurred with paraffin hydrocarbons, whereas

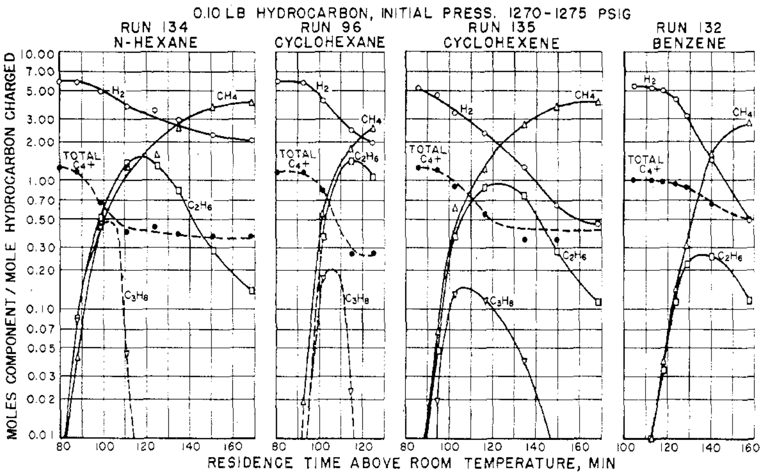

Figure 1. Batch hydrogenolysis of C_6 hydrocarbons

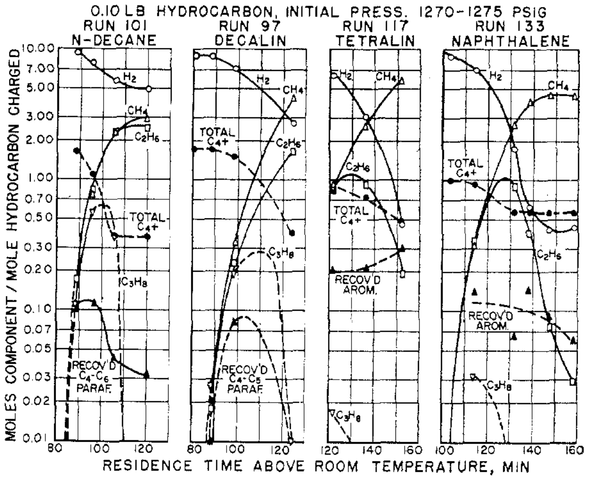

Figure 2. Batch hydrogenolysis of C_{10} hydrocarbons

with increases in feed hydrocarbon thermal stability propane formation decreased sharply. Benzene, Tetralin, and naphthalene showed the lowest propane formations.

The appearance and disappearance of propane and ethane were closely related (Figures 1 and 2). Maximum propane formation occurred after 100- to 110-minute residence time corresponding to reaction temperatures from 1050° to 1100° F., with a tendency for the maximum to occur at higher temperatures with increases in thermal stability (aromaticity) of the feed. As the abundance of propane decreased, the formation of ethane continued and reached a maximum after 120- to 130-minute (140 minutes for benzene) residence time, corresponding to reaction temperatures of 1200° to 1300° F. Methane formation continued until the end of each test, accompanied by rapidly decreasing abundance of ethane and disappearance of propane. The total C_4^+ fraction tended to decrease to a nearly constant amount, probably comprising essentially only the feed hydrocarbon and/or its dehydrogenation, cyclization, and primary cracking products. The final quantity of C_4^+ components increased with increase in unsaturation of the feed hydrocarbon as the result of decrease in the available moles of hydrogen per mole of carbon. This was also reflected in decreases in total feed conversion to C_1 to C_3 paraffins.

Except with benzene feed, equimolar formation of methane and ethane occurred only in the presence of substantial amounts of propane. As soon as propane formation approached maximum, the ethane-methane ratio decreased rapidly. This behavior of the CH_4-C_2H_6-C_3H_8-H_2 system can be better interpreted by considering a batch reactor test of ethane hydrogenolysis (Table III), in which conversion to methane is very low below 1180° F. Thus, initial equimolar methane and ethane formation occurs rapidly via a three-carbon intermediate, of which propane is the stable evidence. As propane disappears with increases in residence time and temperature, hydrogenolysis of ethane takes place and methane is formed at a lesser rate via a two-carbon intermediate, of which ethane is the stable evidence.

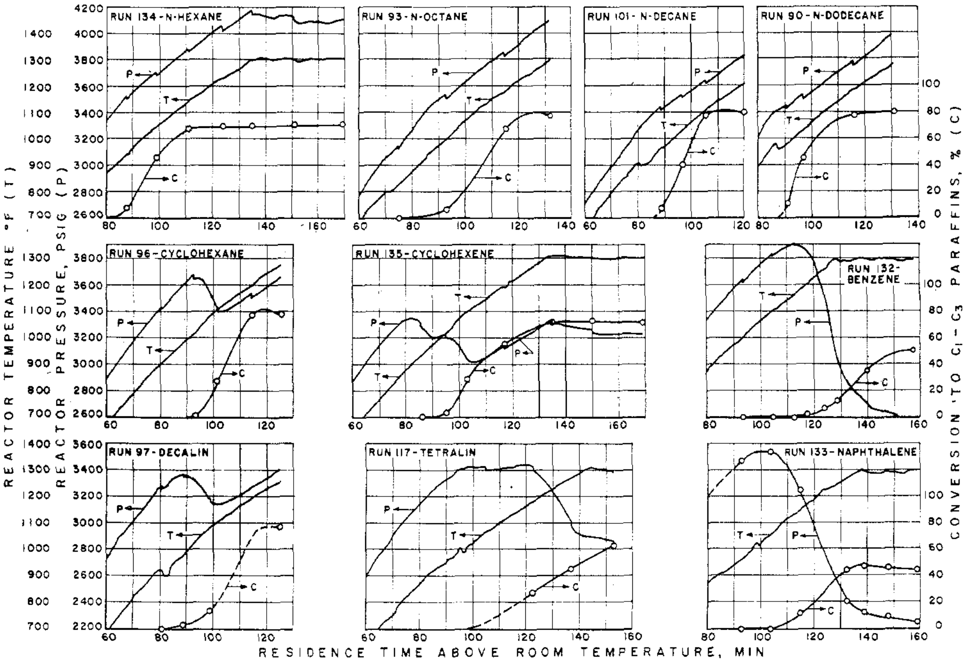

Figure 3. Effects of time and temperature on pressure and conversion

Benzene did not react appreciably with hydrogen below 1150° F.; the small amount of propane formation, and the considerably decreased ethane yield, suggest that temperature conditions were not conducive to three-carbon intermediate formation, and that methane formation proceeded principally through a two-carbon intermediate. Propane and ethane yields during Tetralin and naphthalene hydrogenolysis were intermediate between those from hydrogenolysis of saturated compounds and benzene.

Gaseous product distributions were interpreted on the basis of secondary gas-phase reactions, in agreement with the reaction system employed in a study of hydrocarbon pyrolysis under conditions where primary decomposition reactions are essentially completed (*6*). This system may be expressed as:

$$C_iH_{2i} + H_2 \rightleftharpoons C_iH_{2i+2} \qquad (1)$$

$$C_iH_{2i+2} + H_2 \rightarrow CH_4 + C_{i-1}H_{2i} \qquad (2)$$

where the carbon numbers of the hydrocarbons are $i = 2, 3. . .n$. System 1 was shown to maintain chemical equilibrium over a wide range of pyrolysis conditions. System 2 was far removed from equilibrium, especially in the 1300° F. range, and approached equilibrium very slowly. Although the abundance of the olefinic constituents in the reaction systems described was frequently below the level detectable by routine mass spectrometer analyses because of the normal effect of high pressure on the equilibrium of System 1, the observed sequence of the $C_3H_8 + H_2 \rightarrow CH_4 + C_2H_6$ and $C_2H_6 + H_2 \rightarrow 2CH_4$ paraffin hydrogenolysis reactions seems to support conclusions of the earlier study.

Comparison with Calculated Equilibrium Compositions

Hydrogenolysis equilibrium compositions were calculated with an electronic digital computer for *n*-hexane, cyclohexane, cyclohexene, and benzene feeds from thermodynamic properties compiled by Rossini and others (*11*), assuming ideal gas behavior and no carbon formation. In Table IV, selected results are compared with observed compositions. Equilibrium data indicate that conversion to methane and ethane is virtually complete at hydrogen-hydrocarbon feed ratios approaching the stoichiometric requirements for conversion to methane, but that appreciable amounts of benzene are formed or remain unreacted at lower ratios. Temperature variations over the range used in batch reactor tests have little influence on equilibrium product compositions. Observed compositions indicate a similar degree of approach to the equilibrium compositions, except for run 96 with cyclohexane; the total residence time for this run was substantially shorter than for those with the other C_6 hydrocarbons. As expected, experimental product distributions in all instances show larger amounts of unreacted feed hydrocarbon and hydrogen, smaller amounts of methane, and larger amounts of the ethane intermediate.

Conclusions

The batch hydrogenolysis behavior of a variety of C_6-C_{12} hydrocarbons was defined for initial conditions of 0.070 to 0.074 pound-mole of hydrogen per pound of hydrocarbon (approximately equivalent to stoichiometric requirements for complete conversion of olefins or cycloparaffins to methane) and 1275 pounds per square inch gage at room temperature. Final conditions were determined by attainment of a reactor temperature of 1300° F. at a heating rate of 8° to 10° F. per minute. All hydrogen-hydrocarbon systems, except hydrogen-benzene were characterized by initial equimolar formation of methane and ethane in the presence of relatively high propane concentrations, followed by maximum propane and ethane yields in succession as methane formation increased. Differences in the course of the hydrogenolysis reaction indicated by the rate of pressure rise and drop, rate of formation and disappearance of C_1-C_3 paraffins, and occurrence of breaks in the temperature-time curves could be interpreted on the basis of feed hydrocarbon properties. Ultimate conversion of the feed hydrocarbon to C_1-C_3 paraffins was determined by the carbon-hydrogen charge ratio. Formation of free carbon or of polymerization products was significant only with naphthalene, where only two thirds of

Table II. Batch Hydrogenolysis of Cyclic C_6-Hydrocarbons

	Run 96					Run 135							Run 132							
	Cyclohexane, 0.1008 lb.					Cyclohexene, 0.1007 lb.							Benzene, 0.0999 lb.							
Initial conditions																				
Pressure, lb./sq. inch gage	1275					1275							1270							
Temperature, ° F.	80					71							68							
Hydrogen, lb.-mole	0.007099					0.007236							0.007292							
Hydrocarbon, lb.-mole	0.001197					0.001226							0.001278							
Threshold temp. ° F.	1000[a]					900[a] and 1010[a]							1150[a]							
Gas sample designation	A	B	C	D	E	A	B	C	D	E	F	G	A	B	C	D	E	F	G	H
Residence time above room temp., min.	81	93	102	115	126	86	95	103	117	135	150	169	94	105	113	118	124	129	140.5	158
Pressure, lb./sq. inch gage	3430	3660	3420	3535	3650	3300	3220	3050	3140	3330	3255	3230	3640	3850	3910	3870	3575	3100	2695	2605
Temperature, ° F.	900	1008	1104	1195	1271	930	1017	1093	1190	1307	1299	1297	1003	1105	1165	1205	1256	1295	1299	1295
Total reaction mass, lb.-mole × 10^3	8.392	8.294	7.276	7.106	7.015	7.901	7.256	6.539	6.335	6.272	6.159	6.119	8.277	8.182	8.002	7.730	6.931	5.880	5.104	4.946
Recovered components,[b] moles/mole feed																				
$N_2 + CO + CO_2$	0.038	0.037	0.073	0.057	0.057	0.016	0.019	...	0.033	0.029	...	0.019	...	...	...	...	...	...	...	...
H_2	5.83	5.71	4.11	2.44	1.96	5.17	4.56	3.34	2.35	1.25	0.632	0.451	5.47	5.39	5.24	4.98	4.22	3.19	1.48	0.489
CH_4	...	0.019	0.543	1.74	2.53	0.005	0.066	0.599	1.21	2.69	3.76	4.05	...	0.005	0.011	0.041	0.149	0.311	1.61	2.76
C_2H_6	...	0.006	0.358	1.39	1.04	0.005	0.047	0.362	0.868	0.747	0.278	0.112	...	...	0.011	0.036	0.117	0.221	0.254	0.119
C_3H_8	...	0.006	0.173	0.023	...	...	0.019	0.130	0.117	0.039	0.005	...	0.011	0.011	...	0.010	0.009	0.007	0.003	0.003
C_4H_{10}	...	0.013	0.033	0.006	...	0.005	0.005	0.009	0.019	0.005	...	...	...	...	...	...	...	...	...	...
C_5H_{12}	...	...	...	...	...	...	...	0.004	...	...	...	...	...	...	...	...	...	...	...	...
Cyclohexane	0.435	0.371	0.246	0.040	0.028	...	0.005	0.004	0.014	0.019	0.009	0.005	...	...	...	...	...	...	...	...
C_2H_4	...	...	...	...	...	...	0.005	0.013	0.042	0.010	0.009	0.005	...	...	...	...	...	0.004	...	...
C_3H_6	...	...	...	0.012	...	...	...	0.009	0.014	0.005	...	...	...	...	...	...	...	...	...	...
C_4H_8	...	0.025	0.033	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
C_5H_{10}	...	0.006	0.028	0.012	...	...	...	...	0.009	0.010	0.005	...	...	...	...	...	...	...	...	...
C_6H_{12}	...	...	...	...	...	...	0.005	...	...	...	...	...	...	...	...	...	...	...	...	...
Cyclohexene	...	...	...	...	...	0.005	0.005	0.004	0.014	0.019	0.009	0.005	...	...	...	...	...	...	...	...
Butadiene	...	...	...	...	...	...	...	...	0.005	0.019	...	...	...	...	...	...	...	...	...	...
Benzene	...	...	...	0.006	...	...	...	...	...	0.005	0.009	0.005	0.011	0.011	0.011	0.020	0.018	0.015	0.041	0.027
Total C_4+ components[b,c], moles/mole feed	1.14	1.16	0.821	0.267	0.271	1.25	1.20	0.886	0.538	0.343	0.341	0.360	0.995	0.995	0.996	0.977	0.933	0.870	0.647	0.499
Conversion to C_1-C_3 paraffins[b,d], %	0	0.85	26.8	76.4	76.9	0.26	3.6	28.5	54.9	71.7	72.2	71.2	0.55	0.63	0.53	2.4	6.8	12.9	35.4	50.1

[a] Determined from pressure maximum data.

[b] Calculated from total number of moles of reaction mass and from carbon balance based on composition of recovered components, assuming carbon number of unrecovered components to range from four to six for cyclohexane and cyclohexene feeds, and to be equal to six for benzene feed.

[c] Includes unrecovered C_4+ components. [d] By carbon balance.

Table III. Batch Hydrogenolysis Reactions of Technical Ethane

	Run 36			
Initial conditions				
Pressure, lb./sq. inch gage	505			
Temperature, ° F.	83			
Hydrogen, lb.-mole	0.000983			
Ethane, lb.-mole	0.002863			
Gas sample designation	A	B	C	D
Residence time above room temperature, min.	76	105	123	143
Pressure, lb./sq. inch gage	1170	1320	1420	1810
Temperature, ° F.	757	1024	1180	1299
Total reaction mass, lb.-mole × 10^3	3.846[a]	3.846[a]	3.846[a]	3.437
Recovered components, mole/mole feed				
N_2 + CO_2 + argon	0.045	0.047	0.049	0.023
H_2	0.355	0.329	0.281	0.043
CH_4	0.001	0.007	0.090	1.07
C_2H_6	0.905	0.927	0.907	0.048
C_3H_8	...	0.008	0.004	0.007
i-C_4H_{10}	0.001	0.003	...	...
C_2H_4	0.026	0.023	0.013	0.002
C_3H_6	0.009	...	...	...
Benzene	...	...	...	0.004
Toluene	...	...	...	0.001
Carbon	...	...	...	0.180[c]
Conversion to methane[b], %	0.07	0.34	4.5	53.6
Conversion to carbon[b,c], %	...	...	...	9.0

[a] Assumed equal to total moles of charge.
[b] By carbon balance.
[c] Based on actual recovery of solid deposit; carbon formation due to inadequate supply of hydrogen.

Table IV. Comparison of Observed Product Compositions with Calculated Equilibrium Compositions

	Calculated Equilibrium Compn., Mole %		Observed Compn., Mole %	
	900° K. (1160° F.)	1000° K. (1340° F.)		
n-Hexane. 4090 lb. per sq. inch gage, 6.027 moles H_2/mole (120.5% of stoichiometric[a])			1303° F., 169 min. (run 134)	
H_2	14.64	14.70	H_2	31.3
CH_4	85.33	85.20	CH_4	60.7
C_2H_6	0.04	0.10	C_2H_6	2.1
C_3H_8	0.00	0.00	C_3H_8	...
n-Hexane	0.00	0.00	C_4-C_6	5.6
Cyclohexane	0.00	0.00	N_2 + CO + CO_2	0.3
Benzene	0.00	0.00		
Total[b]	100.01	100.00	Total	100.0
Cyclohexane. 3650 lb. per sq. inch gage, 5.931 moles H_2/mole (98.9% of stoichiometric[a])			1271° F., 126 min. (run 96)	
H_2	1.03	2.32	H_2	33.5
CH_4	98.09	96.56	CH_4	43.1
C_2H_6	0.70	0.81	C_2H_6	17.8
C_3H_8	0.02	0.02	C_3H_8	...
Cyclohexane	0.00	0.00	C_4-C_6	4.6
Benzene	0.16	0.29	N_2 + CO + CO_2	1.0
Total	100.00	100.00	Total	100.0
Cyclohexene. 3230 lb. per sq. inch gage, 5.902 moles H_2/mole (84.3% of stoichiometric[a])			1297° F., 169 min. (run 135)	
H_2	0.80	1.92	H_2	9.0
CH_4	96.06	94.76	CH_4	81.1
C_2H_6	0.87	0.94	C_2H_6	2.2
C_3H_8	0.02	0.03	C_3H_8	...
n-Hexane	0.00	0.00	C_2H_4	0.1
Cyclohexane	0.00	0.00	C_4-C_6	7.2
Cyclohexene	0.00	0.00	N_2 + CO + CO_2	0.4
Benzene	2.25	2.37		
Total[b]	100.00	100.02	Total	100.0
Benzene. 2605 lb. per sq. inch gage, 5.706 moles H_2/mole (63.4% of stoichiometric[a])			1295° F., 158 min. (run 132)	
H_2	0.72	1.74	H_2	12.6
CH_4	89.65	88.49	CH_4	71.3
C_2H_6	0.84	0.91	C_2H_6	3.1
C_3H_8	0.02	0.03	C_3H_8	0.1
Benzene	8.84	8.87	Benzene	12.9
Total[b]	100.07	100.04	Total	100.0

[a] Stoichiometric hydrogen requirement for complete conversion to methane.
[b] Totals in excess of 100.00% due to rounding off of individual component concentrations and characteristics of computation procedure.

the stoichiometric amount of hydrogen required for methane formation was available. This indicates that continuous high-pressure hydrogenolysis of hydrocarbon fuels to fuel gases of high methane content is feasible. However, the formation of nongaseous products of low molecular weight, even when more than the stoichiometric amount of hydrogen for complete conversion to methane is available, appears to be characteristic of the reaction system at practical residence times.

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