

THERMAL SYNTHESIS AND HYDROGASIFICATION
OF AROMATIC COMPOUNDS

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In order to synthesize low sulfur fuels from coal, the Stone & Webster Coal Solution Gasification Process employs the stepwise addition of hydrogen to coal. Enough hydrogen is added in the first step to convert the coal to liquids, which are then hydrogasified to methane, ethane and aromatic liquid products.

Since both these steps involve reactions of aromatic type molecules, the possible chemical pathways involved for their thermal reactions have been studied, along with the kinetics of some of the limiting cases.

Available data show that aromatics are formed by pyrolyzing any of the simple paraffinic hydrocarbons. Formation appears to proceed through the production of olefinic intermediates.

It was felt that a tool in evaluating the relative rate of decomposition of simple aromatics would be their respective delocalization energies, which can be calculated from simple orbital theory. Available kinetic data showed this to be true.

Of the aromatics studied - benzene, diphenyl, naphthalene, phenanthrene, chrysene, pyrene, and anthracene - the rate of decomposition was found to increase in that order. Anthracene decomposes almost 800 times as rapidly as benzene. Further, it was found that the kinetics for the intermediate compounds are ordered inversely with respect to their delocalization energies.

A further consequence of the relation between delocalization energy and kinetics is that the rate of aromatic decomposition should be independent of the hydrogen partial pressure, or the character of the products. Data showed the rate of decomposition of benzene to be independent of hydrogen partial pressure, from 0.1 to 100 atmospheres.

At high hydrogen partial pressures, benzene decomposes primarily to methane, a probable intermediate being cyclohexadiene.

At low hydrogen partial pressures, coke is the final product. The intermediate in this case is probably diphenyl, with coke formation proceeding through stepwise reactions involving diphenyl rather than the progressive addition of benzene molecules. It appears that the conversion of benzene to diphenyl is rapid, and essentially at equilibrium, with the second step, the production of coke from diphenyl, being rate controlling.

Aromatic Synthesis

When pyrolysis is carried out at low pressure - for example, in steam cracking for olefins production, the yield of methane and benzene increases monotonically as severity is increased, until conversion to coke becomes significant.

Early investigations⁽¹⁾ showed that aromatic liquids could be produced from all simple olefins and paraffins. Maximum aromatic yields of 5 wt % were obtained from methane by pyrolysis at 1,050 C for 10 seconds,

(1)

while propane gave a yield of 12% at 850 C. In general, olefins were found to give higher yields of aromatic liquids than paraffins and at lower temperature. For example, at 10 seconds residence time, propylene yielded 19% aromatics at 800 C, compared to 12% at 850 C already noted for propane.

Most investigators concluded that aromatics formed from paraffins during pyrolysis involved, as a preliminary step, the formation of olefins, all olefins from C₂ to C₄ playing a significant role in the synthesis.

Studies also showed that nitrogen acted as a true diluent, reducing the rate by reducing the partial pressure of the reactants. Oxygen enhanced the formation of aromatics from olefins, while hydrogen inhibited aromatization. Since the formation of aromatics proceeded through olefins, it is reasonable to assume that this was a result of the hydrogenation of the olefinic intermediates.

An interesting observation was that reactions leading to the maximum aromatic yield from different light paraffins and olefins generally produced a liquid having about the same composition, i.e.,

40 wt % Monocyclic Aromatic
20 wt % Dicyclic
10 wt % Tricyclic

As conversion progressed beyond peak aromatic conversion, coke was formed, presumably from aromatic precursors.

Figure 1 shows data of Kunugi and Kinney and Crowley relating methane and aromatics yield with ethylene conversion. The data of both investigators form a smooth curve, the former limited to low conversions.

Figure 2 presents similar information for propylene. For both olefins, aromatics and methane production are linear with conversion up to the point of maximum aromatics production. This is shown more clearly on Figure 3 which is a replot of data from the first two figures.

Cracking data for naphtha obtained from the Stone & Webster bench scale pyrolysis unit show this same characteristic relationship. Here a somewhat unanticipated result is that the relationship between methane and aromatics yield is essentially independent of pressure, over a very wide range of pressure conditions.

Some further insight on the effect of hydrogen partial pressure on the formation of aromatics can be found in the work of Moignard⁽²⁾ et al. These experimentors found that under conditions selected for the conversion of light paraffinic hydrocarbons to methane and ethane, there was still a significant production of aromatics. In view of the presumption that aromatics are produced from olefins, this suggested that the hydrogenation of the intermediates to paraffins was not rapid enough to inhibit aromatic formation. Using methane formation as a guide to cracking severity, it is interesting to compare Moignard's data for a light paraffinic naphtha, with other noted earlier.

This is shown on Table 1 (Slide 5). As indicated, the presence of hydrogen does significantly reduce the relative yield of benzene to methane.

Aromatic Decomposition

The remainder of this study was limited to noncatalytic reactions involving relatively small aromatic molecules. Some of the compounds studied are shown on Table 2 (Slide 6). The largest, chrysene, has a hydrogen content of 5.3 wt %, compared to benzene with 7.9 wt % H₂.

The detailed chemical pathway(s) for aromatic molecule hydrogenolysis is unknown, but it is convenient to consider it composed of three steps:

1. Aromatic Ring Destabilization
2. Breakdown to Fragments
3. Fragment Reactions

These are described in turn.

Aromatic Ring Destabilization

The above demarcation stems from the well-known chemical premise that aromatic compounds owe their unusual stability to a delocalization of pi-electrons among the ring molecular framework. To get aromatic molecules to react, the "delocalization energy" must be overcome. Since this energy is large, of the order of 40 kcal/mol, initial destabilization of the aromatic ring is invariably the rate determining step. This argument predicts that the reactivity of all aromatic compounds should be ordered inversely to their delocalization energy. These energies can be computed from simple molecular orbital theory.

Some indication of how this agrees with observation is given in Table 3 (Slide 7), which shows the relative rates at which methyl radicals attack some of the compounds of interest. Notice that all the rates are ordered according to the delocalization energy. The same pattern is observed for a wide variety of reactions, such as free radical attack, nitration and sulfonation. Further, note that benzene and anthracene represent the extremes of reactivity.

A second consequence of the initial destabilization step being rate determining is that, since the further course of reaction exerts little influence on the overall rate, a given aromatic molecule should react at a rate essentially independent of the products being formed. This implies, for example, that rates of benzene decomposition during hydrogenolysis and pyrolysis be comparable even though the products - methane and coke - are strikingly different. This second consequence, while qualitatively true, is not quantitatively as well obeyed as the first.

Breakdown to Fragments

Possible pathways for aromatic decomposition are illustrated on Figure 5 (Slide 8).

The destabilized aromatic ring is a short-lived species which will either revert to the original stable aromatic ring or suffer a breakdown to various fragments. In the latter event, some of the fragments will be nonaromatic and hence subject to more conventional reaction pathways. For example, the destabilized benzene nucleus may go to cyclohexadiene,

or it may go to phenyl, pentadienyl or allyl radicals, which will further pyrolyze or be hydrogenated. For aromatics with multiple rings, e.g., anthracene, the initial breakdown products are very likely to contain smaller aromatic rings, e.g., benzene, in addition to nonaromatic fragments.

Fragment Reactions

The nonaromatic fragments formed from aromatic ring breakdown can undergo a great variety of reactions, among which are: (a) Molecular Reactions, such as simple fission (pyrolysis) or hydrogenation-dehydrogenation reaction; (b) Concerted electrocyclic reactions, for example, fission and rearrangements; (c) Free radical chain reactions such as hydrogenation/dehydrogenation, and polymerization.

The complexity of possible fragment pathways can be reduced by certain generalizations.

Molecular fissions have high activation energies about equal to the strength of the bond being broken. As a result, larger hydrocarbons break much faster than the very smallest. Among the paraffins, the order of stability is methane, ethane, propane, butane, and the approximate fission rate constant for ethane is 0.01; that for butane. Likewise, alkyl benzene or other aromatics containing side chains will tend to lose these much faster than the aromatic nucleus is destabilized.

Electrocyclic reactions, which are concerted, are usually much faster than molecular reactions which involve bond breaking or making.

Free radical chains, when operative, can be much faster than molecular pathways. In our case, at the high temperatures required for hydrogenolysis, free radicals will abound.

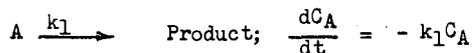
It is probably reasonable to suppose that the hydrogen-olefin-paraffin chain pathways are so fast that equilibrium prevails among these components.

Rate and equilibrium data indicate that the segments of the pathway from benzene fragmentation to ethane formation are expected to be fast relative to benzene destabilization and ethane pyrolysis. A further point to note is that whereas the ring destabilization step (1) is expected to be essentially unaffected by hydrogen, the subsequent product pathways (steps 2 and 3) - whether hydrogenolysis to gas or pyrolysis to coke - should be quite strongly influenced by hydrogen concentration. Finally, multiple-ring aromatics will break down into both nonaromatic and aromatic fragments, of which the former will decompose further by the reactions of step (3), while the latter will tend to lose side chains and go to benzene, the stablest aromatic, which will then further react via the pathway of Figure 5 (Slide 8).

Data Analysis

The essential theoretical hypothesis that aromatic reaction rates are controlled by the ring destabilization step can be tested by comparing the rates of hydrogenolysis and pyrolysis. If the hypothesis is true, the rates of decomposition of a given aromatic compound should be identical for either process. Further, reaction rates and their associated activation energies should correlate with the delocalization energy of that compound.

Sources of experimental information for the aromatic compounds of interest to us are listed in Table 4, along with associated reaction conditions. In each case, the data were processed by the usual simple methods to yield first order rate constants k_1 , sec^{-1} as a function of temperature for the initial decomposition of the aromatic:



It should be noted that the assumption of first order kinetics was not generally verifiable from the data and consequently the precision of these inferred rate constants is not especially good; but the rates are probably of the right order of magnitude in all cases.

Results obtained for benzene and anthracene, theoretically expected to be the extreme cases, are presented on Figure 6 (Slide 9).

Benzene Decomposition Rates

It is apparent that, while the data of separate investigators can each be fitted with straight lines of somewhat different slopes, all the data are adequately described by the single heavy line shown. This indicates that the rates of benzene decomposition during hydrogenolysis and pyrolysis are essentially the same over a rather wide range of experimental conditions. In particular, the insensitivity to hydrogen pressure, which varies from 0.1 atm to 100 atm, is noteworthy. The experimentally observed equality among benzene decomposition rates suggests a common rate-determining step which, in turn, lends support to the thought that aromatic ring destabilization, common to both hydrogenolysis and pyrolysis reactions, is rate-determining.

Benzene Decomposition Products

Some further insight into the reaction pathway can be obtained from the reported reaction products. In the presence of substantial hydrogen, the lowest temperature data (Lang, 900 F) show diphenyl as the sole product, whereas the higher temperature data (Schultz, 980-1,200 F, Dent, 1,100-1,500 F) indicate mainly methane and some ethane as products, with the mole ratio C_2/C_1 tending to unity at benzene conversions below 5%, while approaching zero at high benzene conversion. The diphenyl product suggests either a destabilized ring breakdown to a phenyl fragment or a concerted hydrogen elimination from two benzene molecules. It is also interesting because it represents net dehydrogenation of the benzene for purely kinetic reasons even though thermodynamic equilibrium strongly favors gasification.

None of the above authors report coke (carbon) formation, nor do they mention any hydrogenated C_6 liquid products. However, hydrogen balances on Schultz's data reveal that the empirical formula C_6H_n of the C_6+ components does change from $n=6$ to $n=8$ as benzene conversion proceeds from 0 to 50%, indicating at least some direct hydrogenation of the C_6 ring. In the absence of much hydrogen (pyrolysis), the gaseous reaction products are principally hydrogen and methane. The H_2/CH_4 mol ratio is variable, about 2-4 in Dent's experiments (1,100-1,450 F, 50 atm N_2) and 8-30 in Kinney's case (1,450-2,000 F, 1 atm N_2). Dent also reports small amounts of ethane ($C_1/C_2=1$) at the temperatures of 1,100-1,300 F while Kinney detected traces of acetylene.

Dent makes no mention of coke or condensed products, but Kinney reported diphenyl and carbon (coke) as the major products of benzene pyrolysis and showed further (as shown on Figure 7, Slide 10) that the diphenyl/carbon product ratio decreased in the presence and increased in the absence of coke packing, even though the packing did not appreciably affect the overall benzene decomposition rate. The implications concerning the benzene to diphenyl to coke pathway are, first, that both ring destabilization and breakdown are probably noncatalytic, homogeneous gas phase steps and, second, that the carbon formation reaction is catalyzed by the product, coke, and probably does not involve further benzene participation.

Anthracene Decomposition

The two sources of anthracene decomposition data are Dent and Kinney. For benzene, the coincidence between decomposition rates during pyrolysis and hydrogenolysis also supports the notion that ring destabilization is rate-determining.

Decomposition products from anthracene pyrolysis noted by Kinney were mainly carbon, with the carbon formation catalyzed by coke. Product gases were mainly hydrogen and methane, $H_2/CH_4 = 10$, with traces of acetylene. The hydrogenolysis products noted by Dent were mainly methane and ethane and small aromatic rings, benzene, and naphthalene. No carbon formation was reported. Dent reports only the fraction of anthracene converted to gas. It appears likely that the breakdown of a destabilized anthracene ring, in the presence of

hydrogen, leads to one benzene molecule as a fragment. The gas associated with this initial anthracene breakdown contains methane and ethane in the mol ratios $C_1/C_2 = 3.5$ at 1,200 F and 5.3 at 1,300 F. This does not yield any clear clues about the nonaromatic fragments except, perhaps, that a 4-carbon species (which would give $C_1/C_2 = 2$) may be involved. The change in C_1/C_2 ratio with temperature is too large to be explained by simple ethane pyrolysis with methyl radical hydrogenation.

Other Aromatic Molecules

Decomposition rate data for some of the other aromatic molecules of interest are shown on Figure 8 (Slide 11). Substantially all of the points lie between the anthracene and benzene limits and reasonably straight lines can be drawn to represent the variation of decomposition rate constant vs. temperature for each of the molecules.

Decomposition products observed were as follows:

Diphenyl: During hydrogenolysis at 930 F, 200 atm H_2 , benzene was the sole product. The products of pyrolysis, besides coke, are not clear because the diphenyl results are derived from the benzene pyrolysis data of Kinney.

Naphthalene: During hydrogenolysis at 1,160 F and 200 atm H_2 , Schultz reports methane, ethane and small amounts of propane in the gas with the molal $C_1/C_2 = 1$ at low conversions. Benzene was detected in significant amounts, and traces of toluene and ethylene were also found.

Hydrogen balances indicate some direct hydrogenation of the C₁₀ ring as well, but no coke formation was reported. During pyrolysis, Kinney found the gaseous products are mainly hydrogen and methane with traces of acetylene at 1,500-1,800 F in N₂ at 1 atm. The principal product was solid carbon, and traces of condensation products like 2-2' binaphthyl and perilene were also detected. The binaphthyl is, of course, analogous to diphenyl and suggests an analogous pathway to coke.

Chrysene: Orlow found with 70 atm H₂ that the hydrogenolysis reaction products (by weight) were 25% methane, 35% coke, with the remaining 40% containing phenanthrene, naphthalene, benzene, and various hydrides of each. The pyrolysis products were hydrogen and methane with traces of acetylene in the gas, and solid carbon.

Correlation

The experimental decomposition rate constant data can be fitted by the straight lines shown to yield Arrhenius expressions of the form

$$k_1 = A \exp (-E^*/RT)$$

for each molecule. Values of these Arrhenius parameters, the frequency factor A and activation energy E*, are collected in Table 4 (Slide 12), effectively summarizing the available data.

According to Molecular Orbital theory, the activation energy should be proportional to the delocalization energy, i.e., a plot of E* (experimental) vs. delocalization energy (calculated) should have all molecules lying on the line between the origin and the benzene coordinates. Figure 9 (Slide 13), an arithmetic plot of activation energy vs. delocalization

energy, shows a trend in accord with theory. Anthracene and benzene, the two cases with most data, are in especially good agreement.

Effect of Hydrogen

While it appears that the rate-determining aromatic ring destabilization step is essentially unaffected by hydrogen, the products of decomposition most assuredly are. Increasing hydrogen concentration switches the decomposition pathway from pyrolysis, which leads primarily to solid carbon (coke), to hydrogenolysis, where the product is gas, mainly methane. Understanding how hydrogen concentration controls the crossover between pathways is of interest. However, since the detailed pathway is not explicitly defined, we will focus only on a few aspects expected to be important. Much of the following discussion refers to benzene decomposition, since this case has the most data.

Thermodynamic Equilibrium

It is of interest to examine the equilibrium concentration of H_2 , CH_4 , and C_6H_6 dictated by the following reaction:

	K_p at 1,340 F	
	(a)	(b)
(1) $C_6H_6 + 9 H_2 \longrightarrow CH_4$	10.5	-4
(2) $C_6H_6 \longrightarrow 6C + 3H_2$	16.57	+2
(3) $CH_4 \longrightarrow 2H_2 + C$	1.011	1

where (a) is the exponent to the base 10 and (b) is the power of the pressure term in atmospheres

Calculations for this system show that carbon can always form before benzene has reached gasification equilibrium.

Further, at atmospheric pressure, carbon formation can occur at very low benzene conversions, unless very large excess of hydrogen is used.

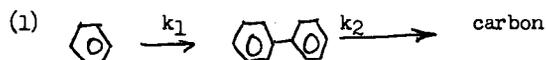
At a fixed hydrogen to benzene ratio, increasing the total pressure favors gasification and retards carbon deposition, based on equilibrium considerations.

A study was therefore made of the effect of total pressure, hydrogen to benzene ratio in the feed, and benzene decomposition on the gross heating value of the product gas. The study was limited to conditions at which ratios of hydrogen to methane in the product gas would be in excess of that required to inhibit the presence of carbon at equilibrium. The results are presented on Figure 10 (Slide 14).

Note that a 15% decomposition of benzene, the maximum heating value that can be obtained at 1,400 F is about 800 Btu/SCF, while at 1,500 F the GHV would be reduced to about 600 Btu/SCF - under conditions where no carbon could exist at equilibrium. The principal curves, i.e., those relating benzene conversion with GHV of product gas, are those for constant pressure and hydrogen to C_6H_6 ratio in the feed. The H_2/C_6H_6 ratios selected for plotting at any given total pressure were those leading to maximum product GHV for a given benzene conversion.

Carbon Formation

Coke is the terminal product of the aromatic pyrolysis pathway and it is of some interest to explore the formation mechanism. Insight into this process is provided by the benzene pyrolysis data of Kinney (1954) in a flow reactor. The diphenyl concentration vs. time behavior reported by Kinney is characteristic of an intermediate in a sequential reaction $A \rightarrow B \rightarrow C$ wherein A (benzene) decreases and C (carbon) increases, both monotonic with time, while the intermediate B (diphenyl) increases at small times and decreases at long times. It is also instructive to compare results at the same temperature, 1,800 F, with and without coke packing as shown in Figure 7 (Slide 10). This further suggests that carbon formation proceeds through a sequence of reactions in series

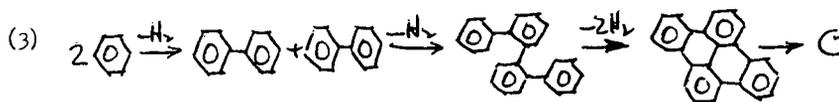


The first reaction is unaffected by coke, whereas the second is catalyzed by coke. Removal of catalyst would slow down the second reaction, thus increasing the intermediate diphenyl concentration as observed.

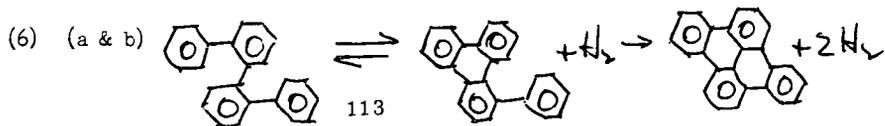
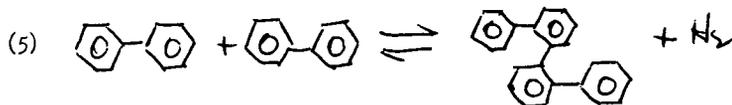
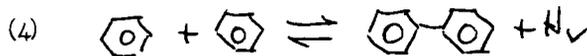
In regard to the molecular reactions leading to carbon, the literature contains many references to a benzene-by-benzene addition with hydrogen elimination (2).

Some of the intermediate products, e.g., diphenyl-benzenes and triphenylene have indeed been detected in the tarry residue resulting from benzene pyrolysis. However, if (2) were the main pathway to carbon, it would

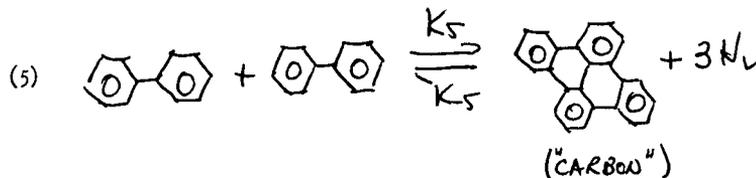
essentially involve benzene in every step and so carbon formation should be very high order in benzene. Catalytic effects enhancing carbon formation should strikingly increase the benzene decomposition rate (and vice-versa). This is not the case as noted above. Further, reactions with benzene in every step would face the maximum benzene delocalization energy barrier compared to reactions between more condensed species with less DE than benzene. Thus, although the concentrations of the condensed species would undoubtedly be lower than benzene, the adverse effect of lower concentration on overall reaction rates could easily be offset by the lower activation energies, and hence higher rate constants, of the more condensed molecules. A plausible alternative scheme for the main pathway to carbon formation is therefore of the form



which involves 1,2,4.... benzene nuclei rather than the 1,2,3.... sequence of (2). According to the above scheme, since the bigger molecules are more reactive, the overall rate should be controlled by the first few steps, namely,



Qualitatively, we can let \bar{C} approximate carbon and since reactions (6) (a) and (b) are intra-molecular hydrogen eliminations which one would expect to be fast compared to the bimolecular hydrogen elimination steps (4) and (5), the reactants of (5) can, in effect, be considered to yield the products of (6b). The essential components of the alternative benzene carbon pathway are thus



of which (4) is a homogenous gas-phase reaction, unaffected by coke, whereas (5) can be catalyzed by coke product.

Kinney's data for benzene pyrolysis to carbon may be modeled by a scheme of two sequential reactions (4) and (5) simplified such that (a) both reactions are kinetically limited in the forward directions and (b) reaction (4) is at equilibrium while (5) is kinetics controlled. Case (b) is the more plausible for the bulk of the data, but some of the experimental trends at low conversions at the lower temperatures are qualitatively as predicted for case (a). A combination of cases (a)

and (b), in which both forward and backward reaction rates are considered for (4) while (5) is assumed kinetics controlled in the forward direction, would probably describe all of Kinney's data adequately.

Finally, we consider the effect of hydrogen on carbon formation. The overall equilibrium, discussed earlier, shows that increasing hydrogen/hydrocarbon ratios and increasing total pressure both retard carbon formation and enhance gasification. Kinetically, however, we have to recognize that there exist at least two types of routes to carbon, namely, by surface reaction and by gas-phase reactions. It is not obvious how these combine. The carbon formation model formulated above is primarily a homogeneous gas phase model and its sensitivity to hydrogen must recognize that the gas-phase route is only one of several possible parallel pathways to carbon. The presence of substantial hydrogen will tend to enhance the back reactions for both (4) and (5) and, clearly, the forward kinetics only, scheme (a), will not be adequate. The maximum conceivable carbon formation that can occur is when reaction (4) is at equilibrium (this gives the maximum diphenyl concentration) and reaction (5) is not retarded by products (even though hydrogen is a product). This, of course, is precisely scheme (b) considered above.

KINETICS OF AROMATIC HYDROGASIFICATION SUMMARY OF EXPERIMENTAL DATA FOR AROMATIC HYDROGENOLYSIS AND PYROLYSIS

Compound	Run Conditions			Press Atm	HC Mol Fr.	Diluent	Reactor	
	Source	Type	Temp, K				Type	Residence, Sec
Benzene	1	H	873-1,123	50	0.10	H ₂	F	60
	1	P	873-1,073	50	0.10	N ₂	F	60
	2	H	800-973	200	0.15	H ₂	B	1,000
	3	P	1,073-1,373	1	0.10	N ₂	F	2-40
	4	H	758	250	0.35	H ₂	B	10 ⁴
Diphenyl	3	P	1,073-1,373	1	0.05	N ₂	F	2-40
	4	H	773	200	0.05	H ₂	B	2x10 ⁴
Naphthalene	2	H	838-958	200	0.10	H ₂	B	1,000
	3	P	1,073-1,273	1	0.02	N ₂	F	2-40
Anthracene	1	H	923-1,073	50	0.04	H ₂	F	60
	3	P	1,073-1,273	1	0.01	N ₂	F	1-40
Chrysene	3	P	1,073-1,273	1	0.005	N ₂	F	2-40
	5	H	723	70	0.13	H ₂	B	10 ⁵

- Sources:**
1. Dent, F.J., 43rd report of the Joint Research Committee, British Gas Council, (1939)
 2. Schultz, E.B. and M.R. Linden, Ind. Eng. Chem. **49**, 2011, (1957)
 3. Kinney, C.R. and E. Delbel, Ind. Eng. Chem. **46**, 548 (1954)
 4. Lang, K. and F. Hoffman, Brenstoff-Chemie **10**, 203 (1929)
 5. Orlow, N.A. and N.D. Lichatschew, Ber., **62B**, 719 (1929)

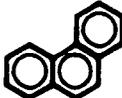
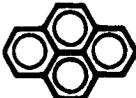
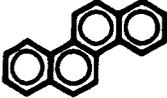
Abbreviations: H- Hydrogenolysis P- Pyrolysis B- Batch F- Flow

Table 1
(Slide 5)

<u>Investigator</u>	<u>Feedstock</u>	<u>Cracked At Press. H₂</u>		<u>Pounds C₆H₆ Per Pound CH₄</u>
Kunugi, et al	C ₂ H ₄	1	No	1.4
Kunugi, et al	C ₃ H ₆	1	No	1.4
Stone & Webster	(Paraffinic	1	No	0.7
Moignard, et al	(Naphtha	10	Yes	0.14

MODEL AROMATIC MOLECULES

KINETICS OF AROMATIC HYDROGASIFICATION

RINGS	NAME	STRUCTURE	FORMULA	T _b , F
1	BENZENE		C ₆ H ₆	176
2	NAPHTHALENE		C ₁₀ H ₈	424
	DIPHENYL		C ₁₂ H ₁₀	491
3	ANTHRACENE		C ₁₄ H ₁₀	646
	PHENANTHRENE		C ₁₄ H ₁₀	643
4	PYRENE		C ₁₆ H ₁₀	740
	CHRYSENE		C ₁₈ H ₁₂	827

KINETICS OF AROMATIC HYDROGASIFICATION REACTIVITY TO METHYL RADICAL ATTACK

<u>COMPOUND</u>	<u>DELOCALIZATION ENERGY</u>	<u>EXPERIMENTAL REACTION RATE RELATIVE TO BENZENE⁽¹⁾</u>
BENZENE	1.155	1
DIPHENYL	1.032	5
NAPHTHALENE	0.904	22
PHENANTHRENE	0.899	27
CHRYSENE	0.833	58
PYRENE	0.755	125
ANTHRACENE	0.632	820

(1) Data from Levy and Swarc, J.A.C.S. 77 1949 (1955)

KINETICS OF AROMATIC HYDROGASIFICATION

ARRHENIUS PARAMETERS FOR AROMATIC DECOMPOSITION RATES

<u>COMPOUND</u>	<u>A</u> Sec ⁻¹	<u>E*</u> Kcal/Mol	<u>T^{1/2}(1,000 °K)</u> Half-life, Sec
BENZENE	4.4x10 ⁸	52.6	499
DIPHENYL	1.6x10 ⁷	43.1	118
NAPHTHALENE	4.5x10 ⁵	36.8	171
CHRYSENE	3.4x10 ⁵	33.5	43
ANTHRACENE	1.8x10 ⁵	30.7	20

Note: $k_1 = A \exp(-E^*/RT)$

$$T_{1/2} = \text{half-life} = (0.693/k_1)$$

PYROLYSIS OF ETHYLENE

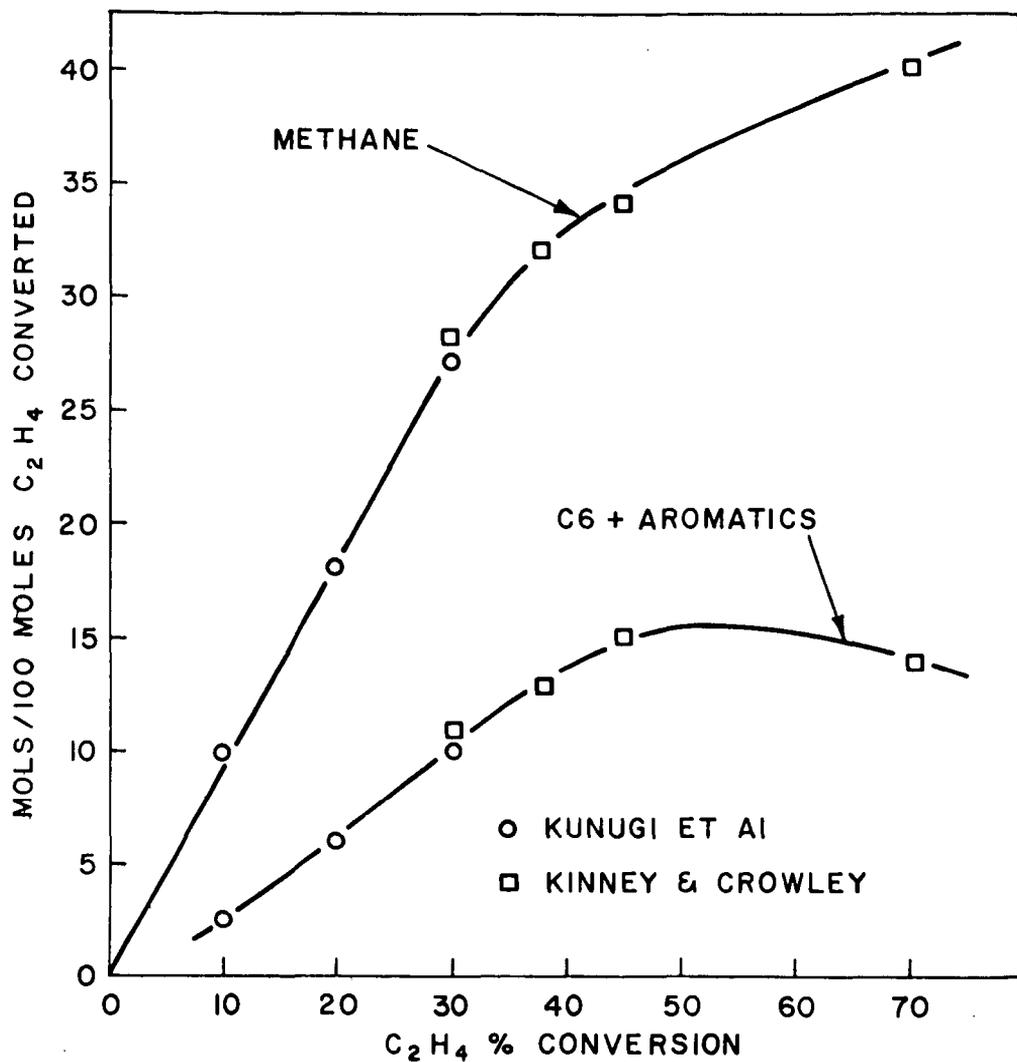
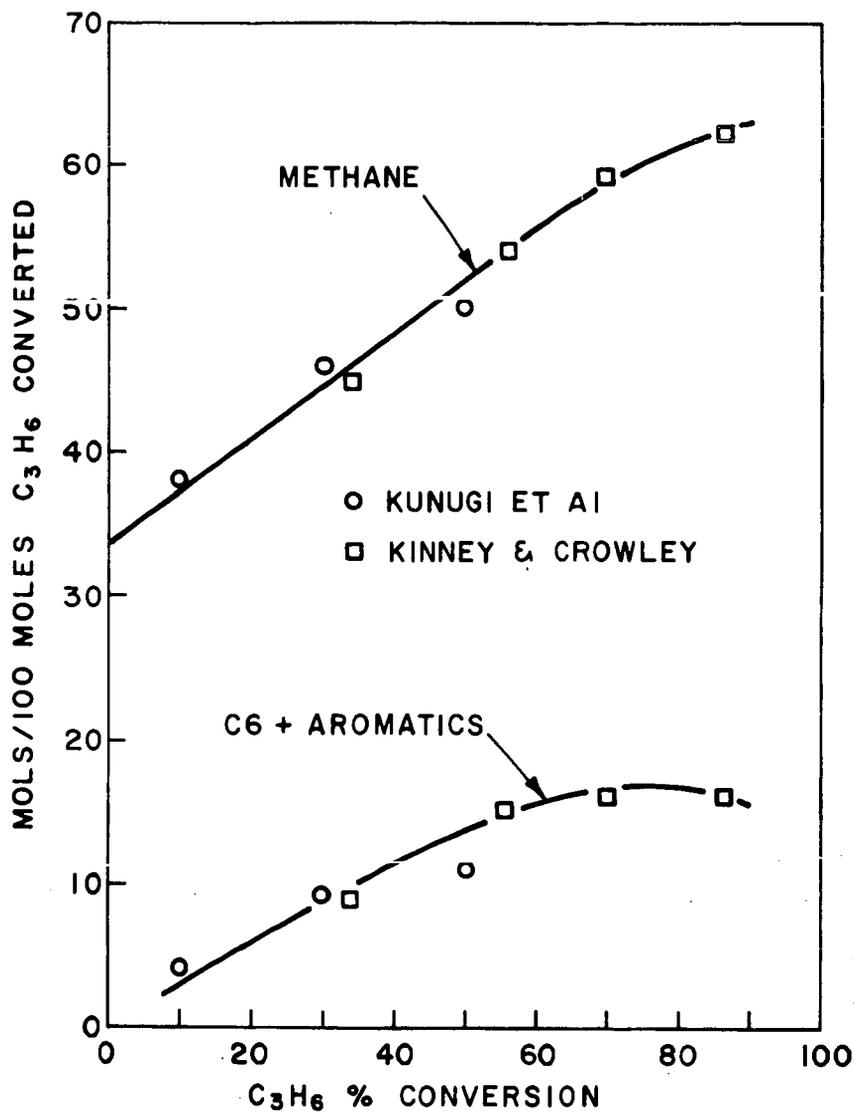


Figure 2
(Slide 2)

PROPYLENE PYROLYSIS



ETHYLENE & PROPYLENE PYROLYSIS (YIELDS AS % FEED CONVERTED)

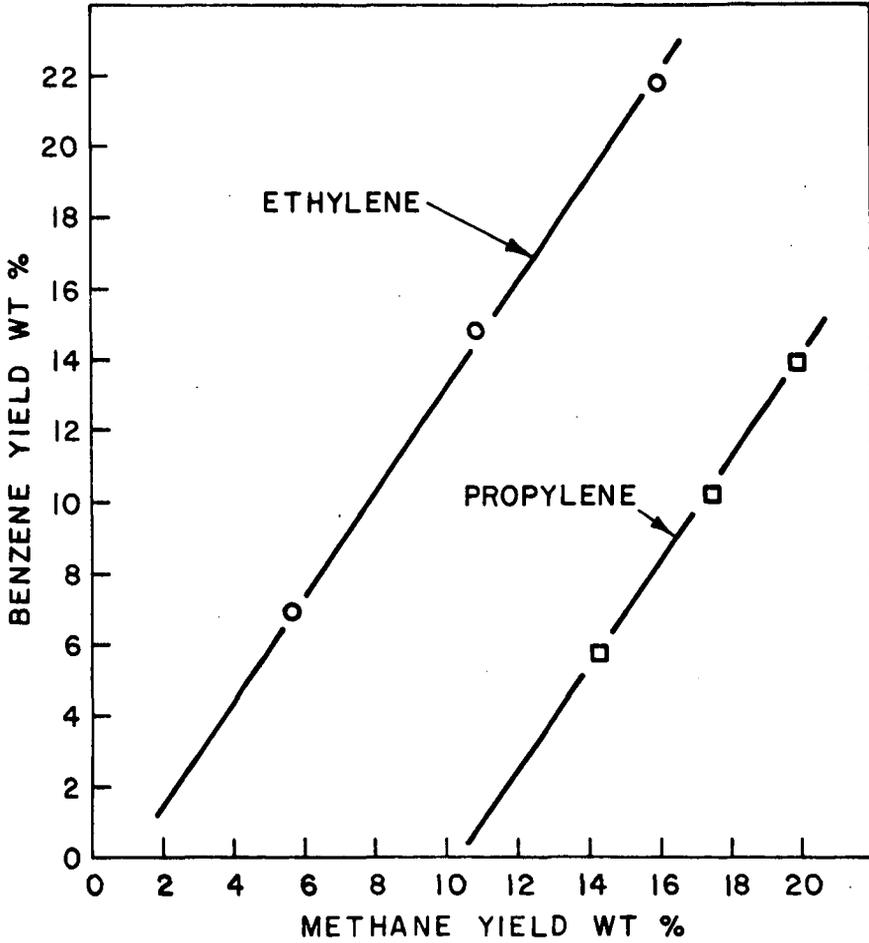


Figure 4
(Slide 4)

NAPHTHA PYROLYSIS

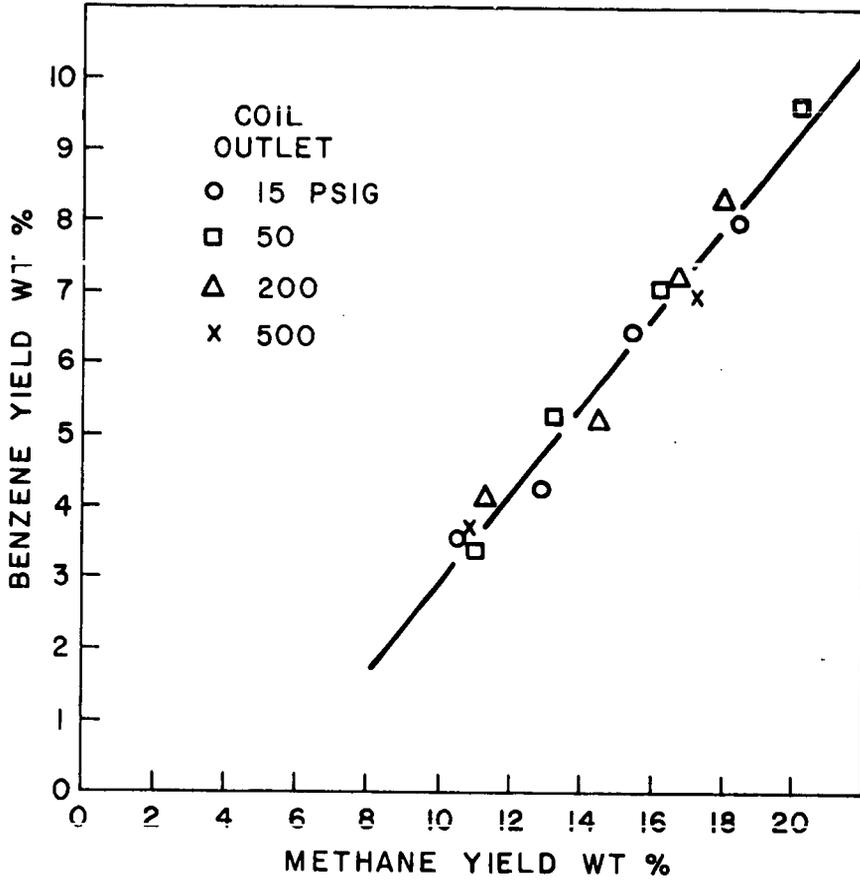


Figure 5
(Slide 8)

BENZENE HYDROGENOLYSIS PATHWAYS

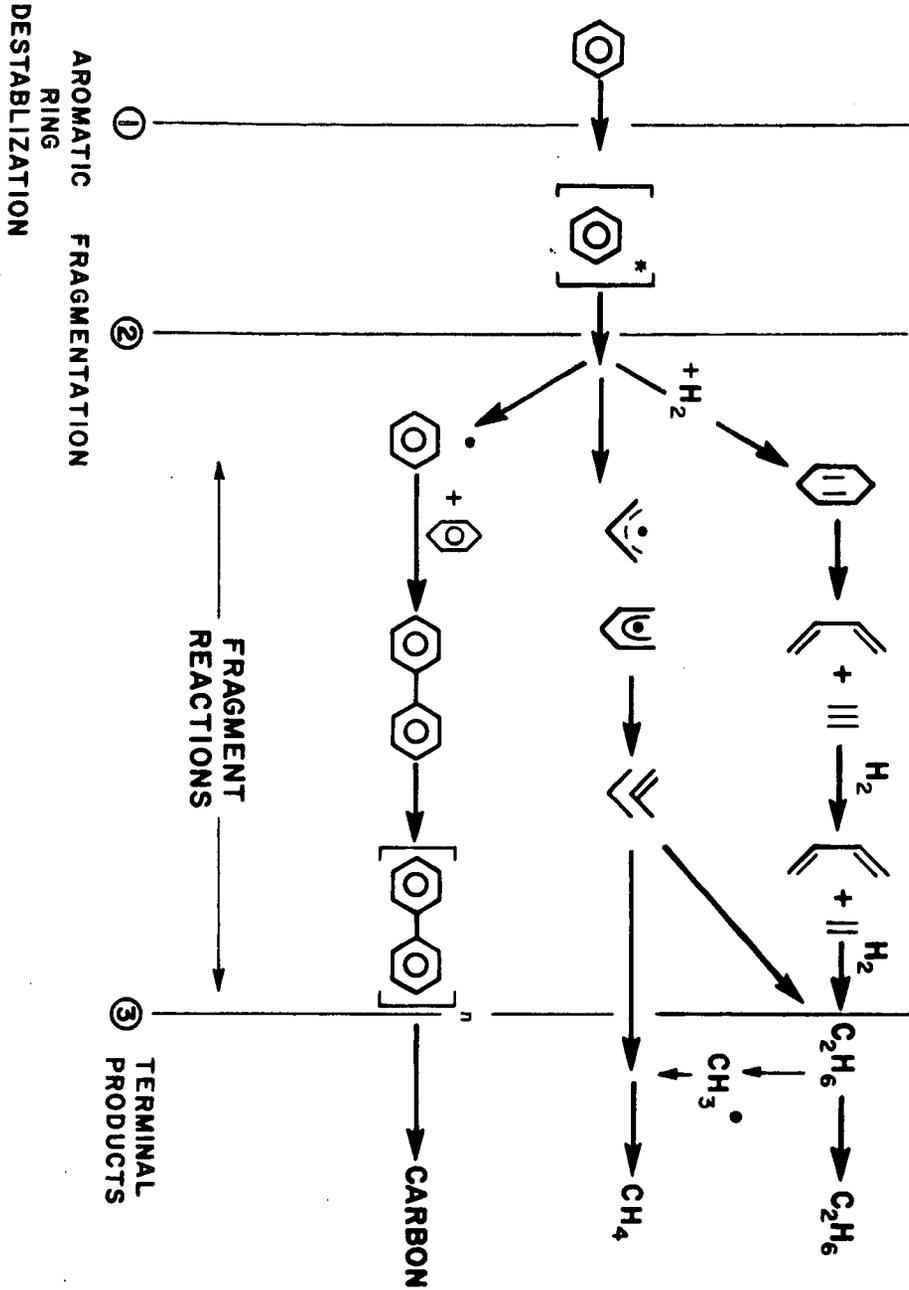
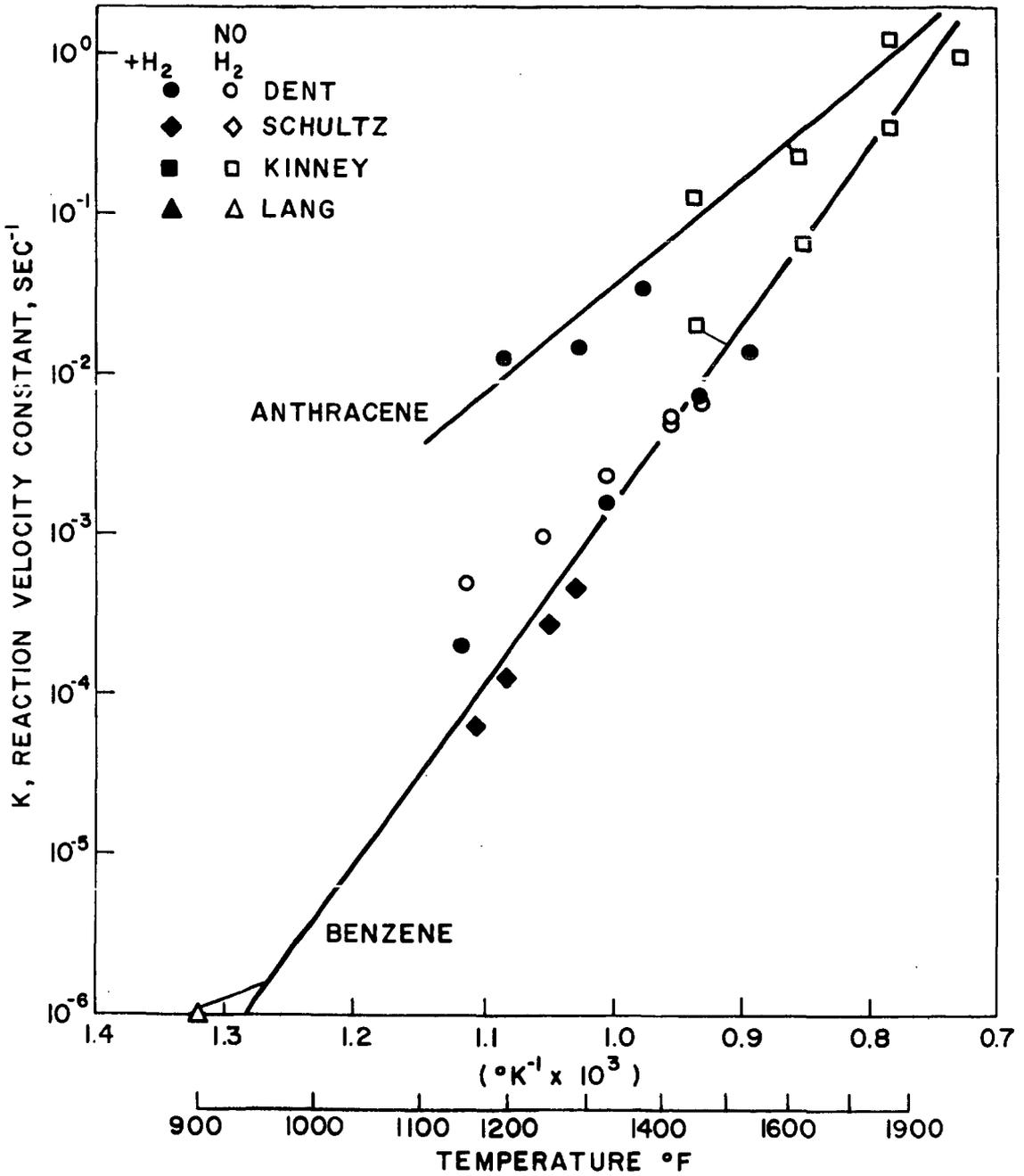
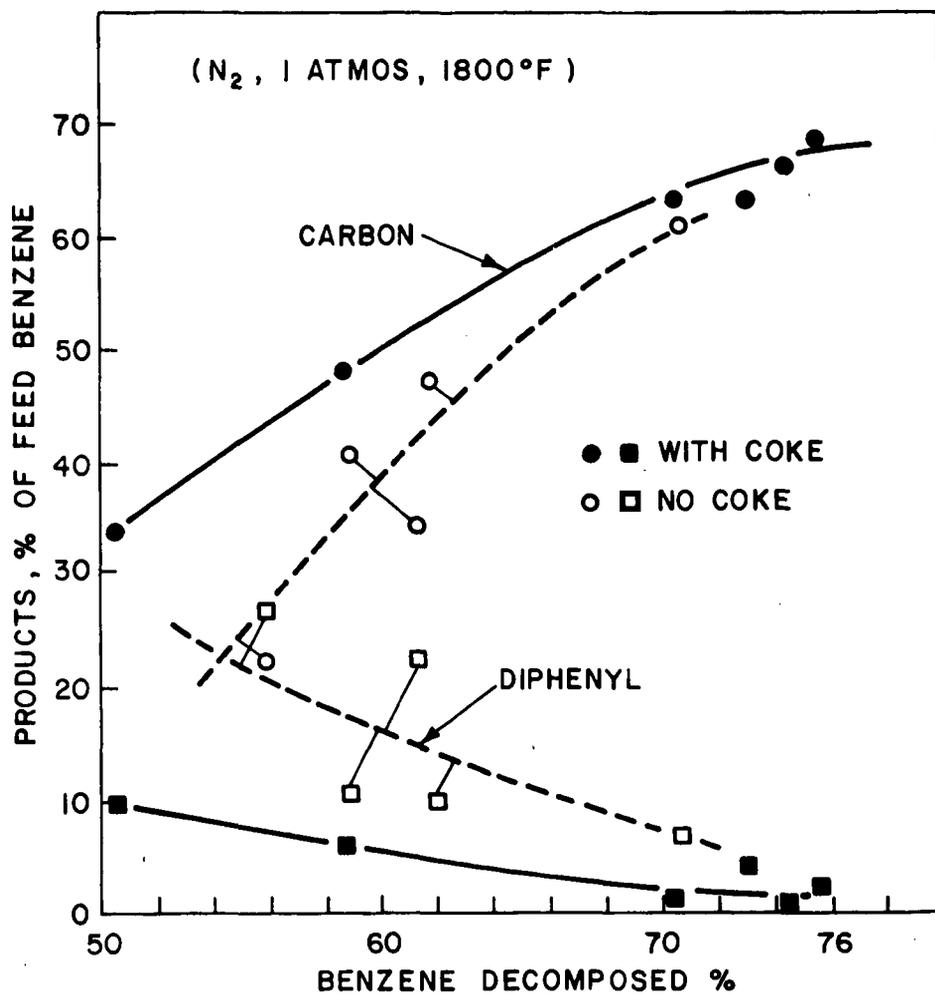


Figure 6
(Slide 9)

RATES OF DECOMPOSITION FOR BENZENE AND ANTHRACENE

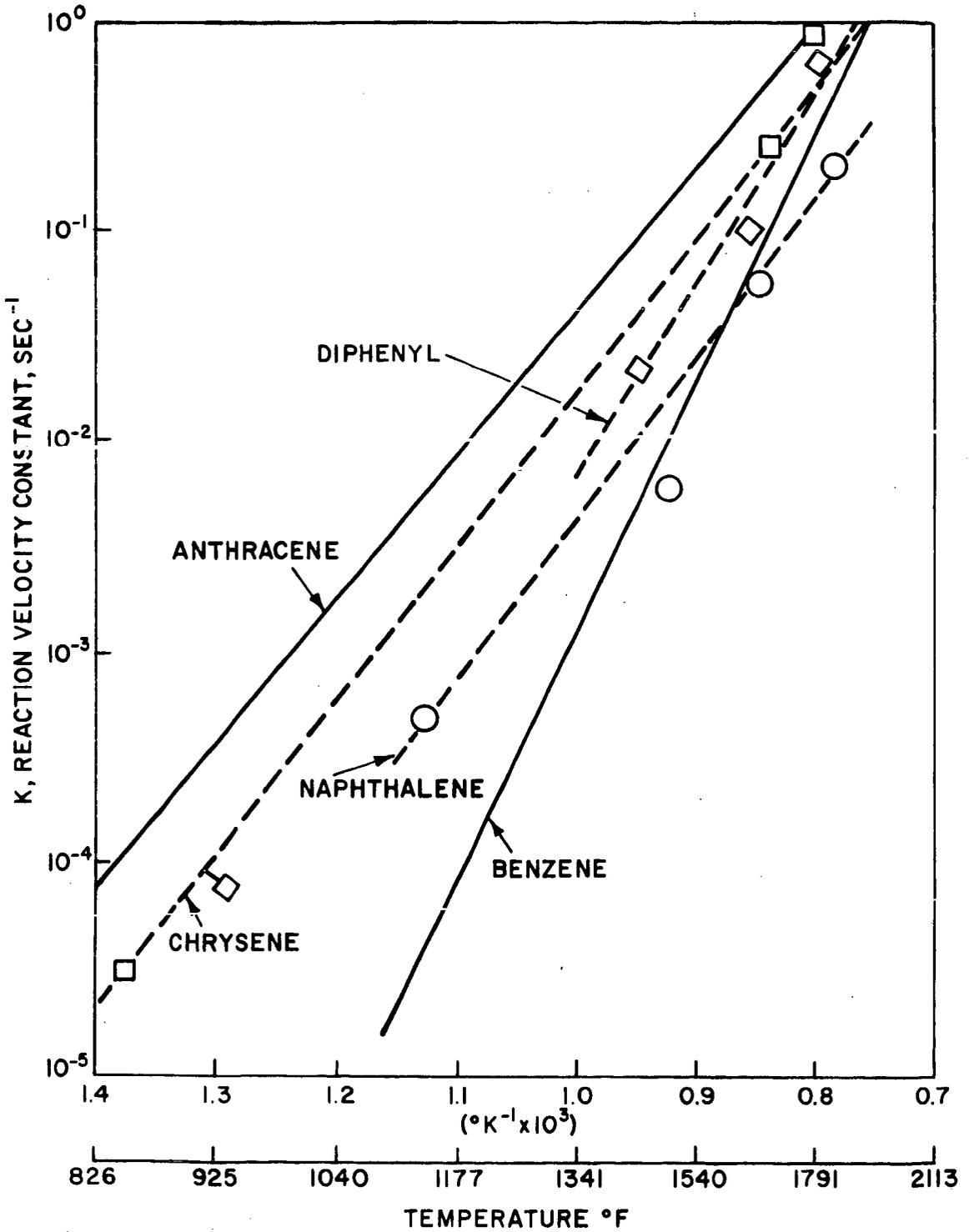


EFFECT OF COKE ON PRODUCT DISTRIBUTION FOR BENZENE PYROLYSIS



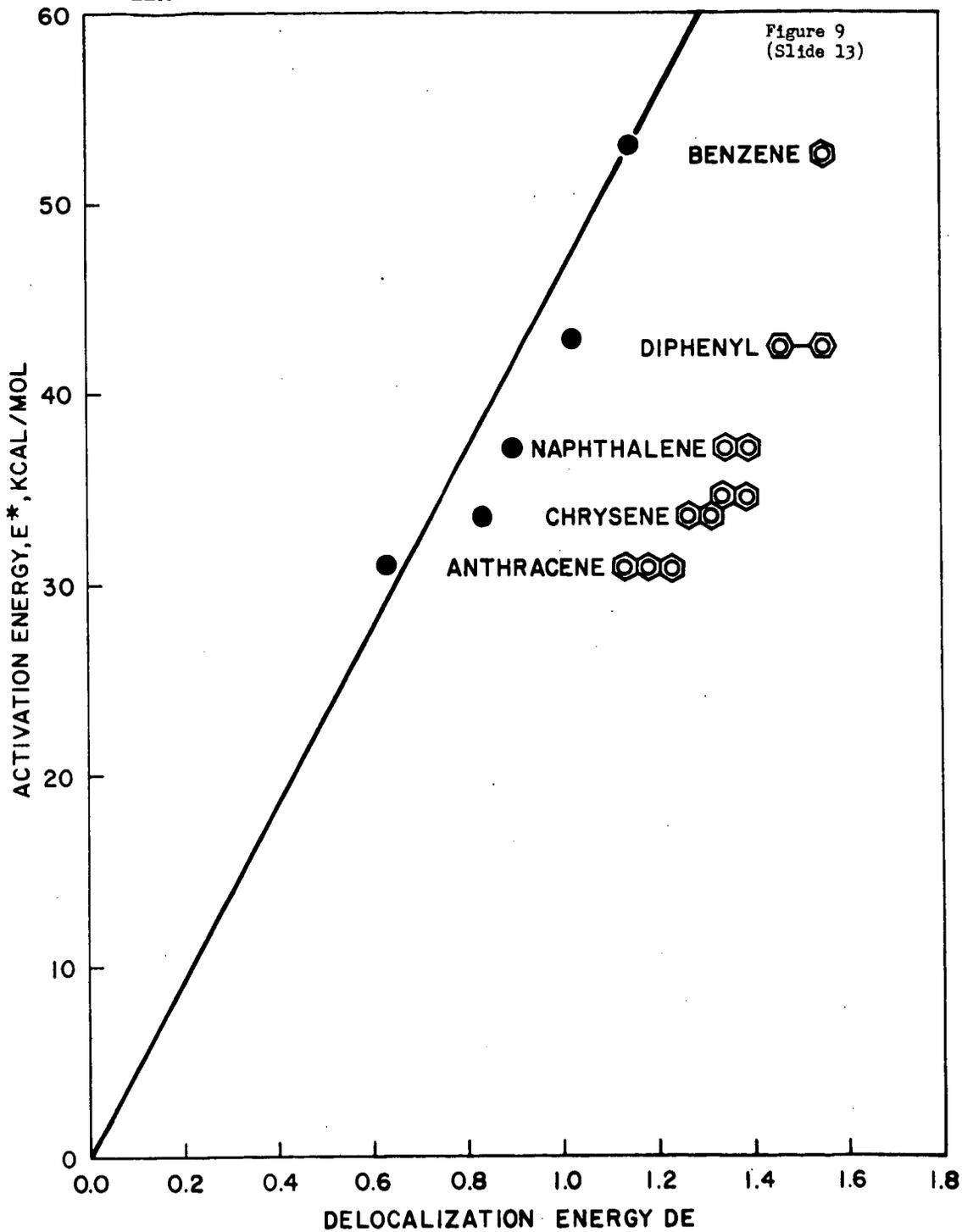
DECOMPOSITION RATES FOR SELECTED AROMATICS

Figure 8
(Slide 11)



RELATION BETWEEN ACTIVATION AND DELOCALIZATION ENERGIES

Figure 9
(Slide 13)



EFFECT OF OPERATING VARIABLES ON GASIFICATION OF AROMATICS

Figure 10
(Slide 14)

