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**THE RADIOLYTIC AND PYROLYTIC DECOMPOSITION
OF ORGANIC COOLANTS**

VII. THE PYROLYSIS OF HIGH BOILING RESIDUE

by

G. JUPPE and H. RAU

1966



ORGEL Program

Joint Nuclear Research Center
Ispra Establishment - Italy

Chemistry Department
Organic Chemistry

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SUMMARY

The kinetics of the thermal decomposition of high boiling residue originating from the in-pile radio-pyrolysis of OM-2 were studied and compared with the kinetics of the thermal decomposition of pure m-terphenyl. At low conversions the rate of decomposition of high boiling residue was found to be approximately seven times faster than the rate of formation of high boilers from m-terphenyl. The main reaction products of the high boiler decomposition were benzene and diphenyl. There were no terphenyl isomers formed. The rate of the total gas production was about 100 times greater from high boiling residue than from m-terphenyl. There were more saturated and unsaturated aliphatic hydrocarbons and less hydrogen produced.

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K E Y T O T H E T A B L E S

TABLE 1 COMPOSITION OF REACTION PRODUCTS

K E Y T O T H E F I G U R E S

FIG. 1 TOTAL GAS FORMATION
FIG. 2 TOTAL GAS COMPOSITION
FIG. 3 BENZENE PRODUCTION
FIG. 4 DIPHENYL PRODUCTION
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The thermal decomposition of o-, m-, and p-terphenyl as well as commercial terphenyl coolant mixtures results mainly in the formation of hydrogen, saturated and unsaturated aliphatic hydrocarbons, benzene, toluene, xylenes, diphenyl, terphenyl isomers, quater-, quinqa-, hexa- and higher polyphenyls. A kinetic description of the thermolysis of terphenyls can only be done accurately at extremely low conversion rates i.e. at the beginning of the reaction where only the decomposition of terphenyl has to be considered. At higher conversion rates the pyrolysis of terphenyls is complicated by consecutive reactions of the above mentioned reaction products; also benzene, diphenyl, quater-, quinqa-, hexa- and higher polyphenyls are then thermally degraded and also these processes lead to the same species of reaction products as the thermal decomposition of terphenyl itself: benzene, diphenyl, terphenyl isomers and higher polyphenyls could be formed.

The free energies of formation of benzene, diphenyl, terphenyls, quater- and higher polyphenyls from elemental carbon and hydrogen are positive at all temperatures so that these compounds are actually unstable with respect to their elements. From this follows that there can never any equilibrium be obtained between forward and backward reactions in the organic coolant; at infinite pyrolysis times all thermal decomposition processes, being primary or consecutive, will finally lead to only hydrogen and carbon formation.

In the present investigation we tried to evaluate to what extent the thermal decomposition of polyphenyls leads to a reformation of di- and terphenyls. In addition to this the kinetics of the thermal decompositions of polyphenyls were compared with that of m-terphenyl and the differences in the nature and the yield of all decomposition products from these two degradations established.

Manuscript received on August 3, 1966.

1 - I N T R O D U C T I O N

The thermal decomposition of diphenyl and the three terphenyl isomers is well studied¹⁾²⁾.

The rates of decomposition and the yields and nature of reaction products show slight differences between the different compounds, biphenyl being most stable followed by p-, m-, and o-terphenyl. With the exception of p-quaterphenyl³⁾ no research was reported on higher polyphenyls.

It is generally assumed, although not strictly proven, that the heat resistance of polyphenyls decreases with increasing molecular weight.

K.J.A. Singer and coworkers⁴⁾ studied briefly the pyrolysis of high boiling residue originating from the thermal decomposition of Santowax R and consisting mainly of a mixture of polyaromatic compounds. The rate of decomposition in the initial polymer was about three times less than the decomposition of pure Santowax at identical pyrolysis conditions. Benzene and diphenyl were the main reaction products: no terphenyls were found. Approximately three times more gas was formed during the polyphenyl pyrolysis than during the pure terphenyl decompositions.

1) G. Juppe, M. Alvarenga, H. Hannaert, Euratom Report EUR 1647.e

2) A.W. Boyd, J.Nuclear Materials 9, 1 (1963)

3) R.O. Bolt, J.G. Carroll, B.J. Fontana, USAEC Report
TID-7007 pt 1 and 2 (1957)

4) K.J.A. Singer, H. Christensen, E. Larsen,
Atomkernenergie 7, 396 (1962)

2 - MATERIALS AND METHODS

2.1 - MATERIALS

For the preparation of polyphenyl residue preirradiated OM-2 was used. The sample had previously been radiopyrolyzed in a loop experiment at the Melusine reactor, Grenoble, France; as total dose 9,9 Wh/g at 400°C were received. The composition was 2,6% diphenyl, 14,9% o-terphenyl, 44,5% m-terphenyl, 2,5% p-terphenyl and 35% highboiling residue.

The sample was extracted with heptane-toluene in a three to one mixture. The black solid residue used for our experiments contained 0,3% o-terphenyl, 0,7% m-terphenyl, 0,15% p-terphenyl, 0,15% quaterphenyls, triphenyl-benzenes and triphenylene, and 98,7% highboiling residue. The average molecular weight was 1500-2000.

2.2 - PYROLYSIS

The preparation of the samples and the pyrolysis were carried out as previously described¹⁾.

The chosen temperatures of 425°C, 440°C and 455°C were measured continuously by thermoresistance and did not fluctuate more than $\pm 1^\circ\text{C}$ around the set point.

2.3 - ANALYSIS

The determination of the total gas was performed in a conventional gas line as previously described¹⁾. Benzene and low boilers had been separated before condensing them in a carbon dioxide/acetone mixture. The mass spectroscopic analysis of hydrogen, methane, ethane, ethylene, acetylene, propene, propylene, n-butane, i-butane, isobutylene, n-pentane and i-pentane were performed on an Atlas CH₄ spectrometer²⁾.

The gas chromatographic analyses for benzene, diphenyl, the three terphenyl isomers, the quaterphenyl isomers and the high boilers were carried out by injecting trichlorobenzene solutions containing an inner standard. A 2,50 m CsCl-column was used. The raise in temperature over a 150°C range was maintained at 20°C per second.

3 - RESULTS

3.1 - FORMATION OF GASES

A comparison of the total gas formation during the pyrolysis of the polymer at 425°C, 440°C and 455°C is given in fig. 1. The rates of the formation of the individual gases hydrogen, methane, ethane, ethylene, acetylene, propane, propen, n-butane, i-butane, 1-butene, 2-butene are described in fig. 2.

3.2 - FORMATION OF LIQUIDS

A comparison of the experimental data for the formation of benzene from the 425°C pyrolysis of highboiling residue and of m-terphenyl is given in fig. 3. In fig. 4 are compared the experimental data of the diphenyl formation from high boilers and from diphenyl. The rates of disappearance of the o-, m-, and p-terphenyl are shown in fig. 5. The kinetics of the formation of quaterphenyls from highboiling residue and from m-terphenyl are compared in fig. 6. The decrease of highboiling residue from the high boiler experiment is compared in fig. 7 with the formation of high boilers when pyrolyzing m-terphenyl at the same reaction conditions.

Table 1 shows the composition of the liquid phase after 23 hours pyrolysis time at 425°C for both the high boiler and m-terphenyl pyrolyses.

TABLE 1 - COMPOSITION OF REACTION PRODUCTS (wt.%)

| | HIGH BOILING RESIDUE | m-TERPHENYL |
|---------------|-----------------------------|---------------------------|
| BENZENE | 1,48 | 0,09 |
| DIPHENYL | 0,44 | 0,18 |
| o-TERPHENYL | 0,30 (-0,04 ^a) | 0,02 |
| m-TERPHENYL | 0,82 (-0,01 ^a) | 99,3 (-0,7 ^a) |
| p-TERPHENYL | 0,08 (-0,06 ^a) | ---- |
| QUATERPHENYLS | 0,15 (+0,04 ^b) | 0,19 |
| HIGH BOILERS | 97,92 (-2,18 ^a) | 0,38 |

a) decrease during the experiment

b) increase during the experiment

4 - DISCUSSION

4.1 - FORMATION OF GASES

4.1.1 - TOTAL GAS

From the pyrolysis of highboiling residue approximately 100 times more total gas is evolved than from the thermal decomposition of m-terphenyl. The formation follows a higher than zero order kinetics.

4.1.2 - INDIVIDUAL GASES .

At the beginning of the reaction, for each 100 molar parts of hydrogen formed there are 85 parts methane, 27 parts ethane, 9 parts propane, 5 parts n-butane, 5 parts i-butane, 1 part n-pentane, 40 parts ethylene, 20 parts acetylene, 3 parts propene, 18 parts 1-butene and 10 parts 2-butene. The composition of the total gas being evolved during the m-terphenyl pyrolysis differs very much from the above figures: per 100 parts hydrogen, 4 parts methane, 1 part ethane, 0,1 part propane, 0,04 parts n-butane, 0,01 parts i-butane, 0,01 parts n-pentane, 3 parts ethylene, 1 part acetylene, 0,2 parts propene, 0,1 part 1-butene, 0,05 parts 2-butene are formed.

4.1.2.1 - HYDROGEN

The high boiler pyrolysis yields 32% hydrogen after one hour at 425°C. The hydrogen percentage increases to 40% after five hours pyrolysis time at the same reaction conditions. The hydrogen percentage of the total gas originating from the thermal decomposition of m-terphenyl is about three times higher and stays constant even at longer pyrolysis times.

4.1.2.2 - SATURATED ALIPHATIC HYDROCARBONS

Initially the pyrolysis of highboiling residue forms 9 times more methane, 10 times more ethane, 10 times more propane, 50 times more n-butane, 50 times more i-butane and 9 times more pentanes than are formed during the thermal decomposition of m-terphenyl. When pyrolyzing highboiling residue six hours, instead of one, at 425°C, 20% more methane, ethane and butane are formed. The yields of n-butane, i-butane and the pentanes remain even at prolonged pyrolysis times roughly constant.

4.1.2.3 - UNSATURATED ALIPHATIC HYDROCARBONS

At the beginning of the pyrolysis of highboiling residue, 4 times more ethylene, 2 times more acetylene, 4 times more propene, 12 times more 1-butene, 10 times more 2-butene and 12 times more pentenes are formed than under identical reaction conditions in the m-terphenyl pyrolysis.

The yield of all unsaturated aliphatic hydrocarbons is strongly decreasing with increasing reaction times. After six hours only one third of the initial content of ethylene, one third acetylene, one half propene, one half 1-butene, one half 2-butene is found. The percentages of the unsaturated hydrocarbons being formed during the m-terphenyl pyrolysis show nearly no change between short and long reaction times.

4.2 - FORMATION OF LIQUIDS

4.2.1 - BENZENE AND DIPHENYL

The formation of benzene and diphenyl can be described as resulting from a higher than zero order reaction. This is in contrast to the formation of benzene and diphenyl from the thermal decomposition of terphenyls, where a zero order reaction rate is observed¹⁾.

Compared with the thermal decomposition of m-terphenyl 30 times more benzene and about 9 times more diphenyl are formed at the beginning of the high boiler pyrolysis.

A molar ratio of 1,6 to 1 for the benzene/diphenyl formation is observed for the high boiler pyrolysis compared with a 1,2 to 1 ratio for the m-terphenyl pyrolysis.

4.2.2 - o-, m-, p-TERPHENYL

Up to 4% conversion of the highboiling residue no formation of terphenyls can be observed.

4.2.3 - QUATERPHENYLS, TRIPHENYLBENZENES AND TRIPHENYLENE

A very small portion (0,04%) of the pyrolysis products from highboiling residue consists of quaterphenyls, triphenylbenzenes and triphenylene. A much higher percentage (0,2%) of these compounds is formed under identical reaction conditions when pyrolyzing m-terphenyl.

4.2.4 - HIGH BOILERS

The decrease of the starting material can be reasonably well described as resulting from a first order reaction. At the same reaction conditions and at the beginning of the pyrolysis approximately 13 times more high boilers disappear during the high boiler pyrolysis than are formed during the m-terphenyl pyrolysis.

5 - C O N C L U S I O N S

The following conclusions can be drawn from our investigation:

a) The back reaction of the terphenyl pyrolysis i.e. the reformation of terphenyls from highboiling residue is practically non existent.

b) The over-all decomposition rate of the 425°C pyrolysis of highboiling residue is approximately seven times higher than that of m-terphenyl.

c) Approximately 52 wt.% of the over-all decomposition products formed during the high boiler pyrolysis are benzene. The rate of the benzene production from highboiling residue is approximately 30 times higher than the rate of benzene production during the m-terphenyl pyrolysis.

d) The kinetic data obtained for the benzene formation during the high boiler pyrolysis indicate that the benzene production during the thermal decomposition of terphenyls is actually a higher than zero order reaction. The observed zero order rate during the m-terphenyl pyrolysis is due to benzene production from both high boiler and m-terphenyl decomposition. The rate of benzene production from terphenyl decreases with pyrolysis time and the rate of benzene production from the decomposition products increases with time, due to increased amount of decomposition products present. The approximate zero order kinetics observed for the formation of benzene during the terphenyl pyrolysis is a result of the balancing of these two production rates.

e) Approximately 18 wt.% of the over-all decomposition products of the high boiler pyrolysis are diphenyl. The rate of biphenyl production is about seven times higher than found for the diphenyl formation from the m-terphenyl pyrolysis.

f) The kinetic data obtained for the diphenyl formation during the high boiler and the terphenyl pyrolysis indicate that the diphenyl production during the thermal decomposition of terphenyls must also be a higher than zero order reaction.

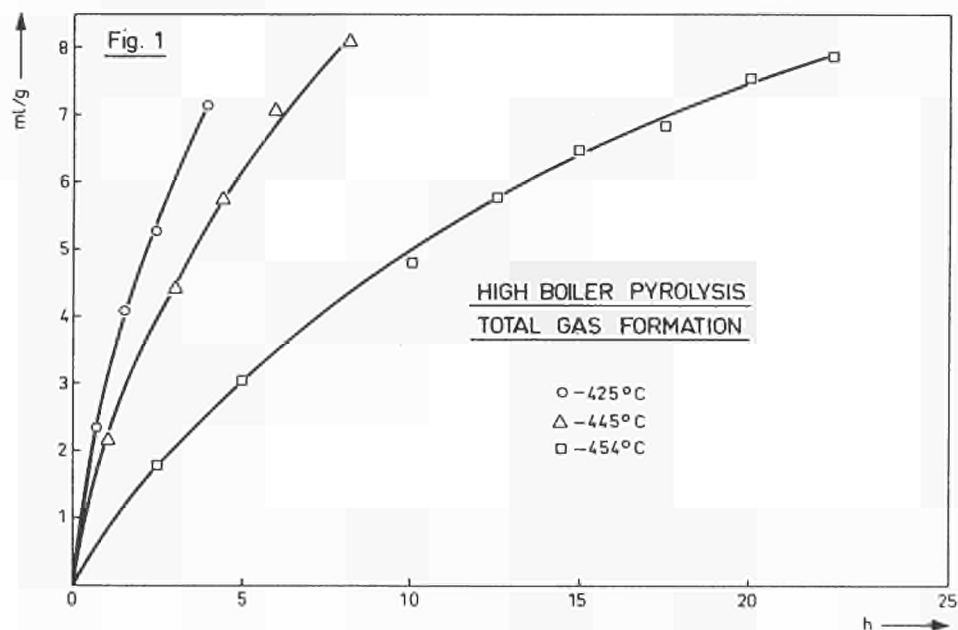
g) About 100 times more gas is formed when pyrolyzing highboiling residue instead of terphenyls. The total gas contributes about 25 wt.% of the over-all decomposition products.

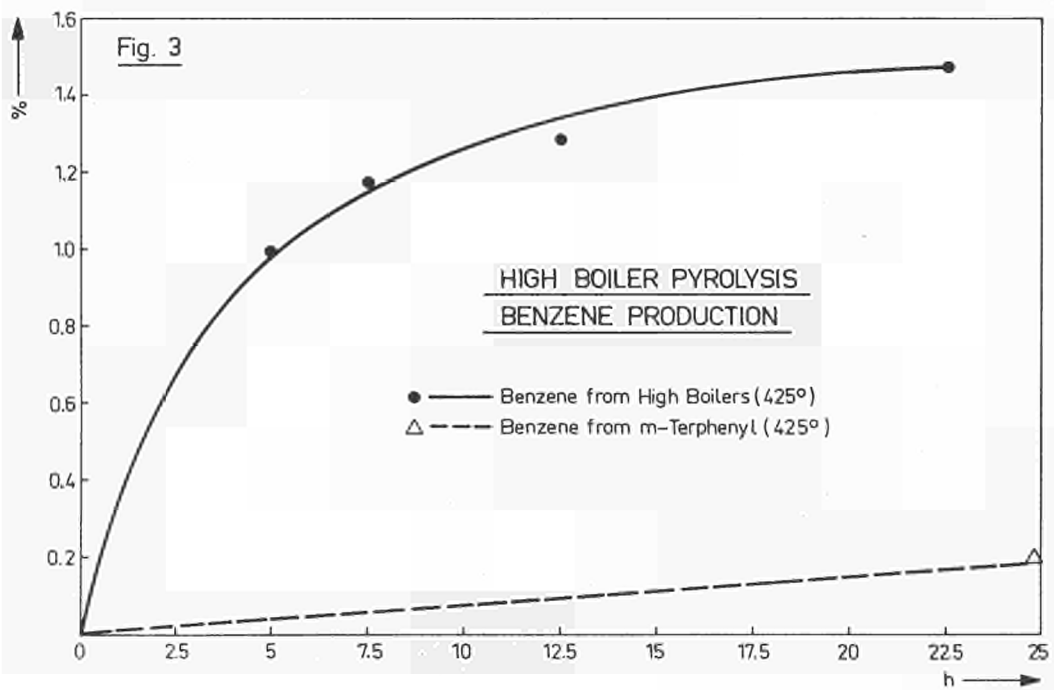
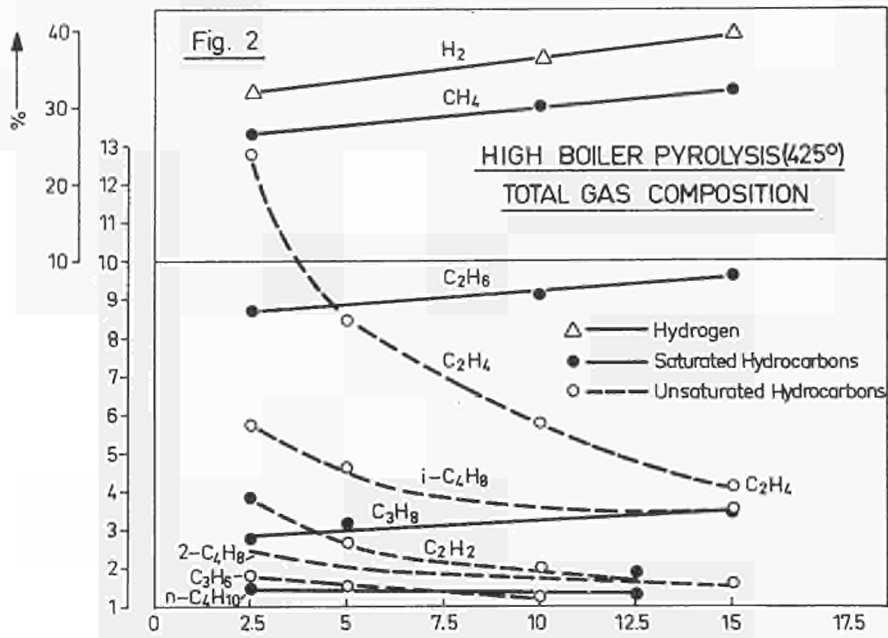
h) The kinetic data obtained also indicate that the total gas formation from terphenyls must actually be a higher than zero order reaction.

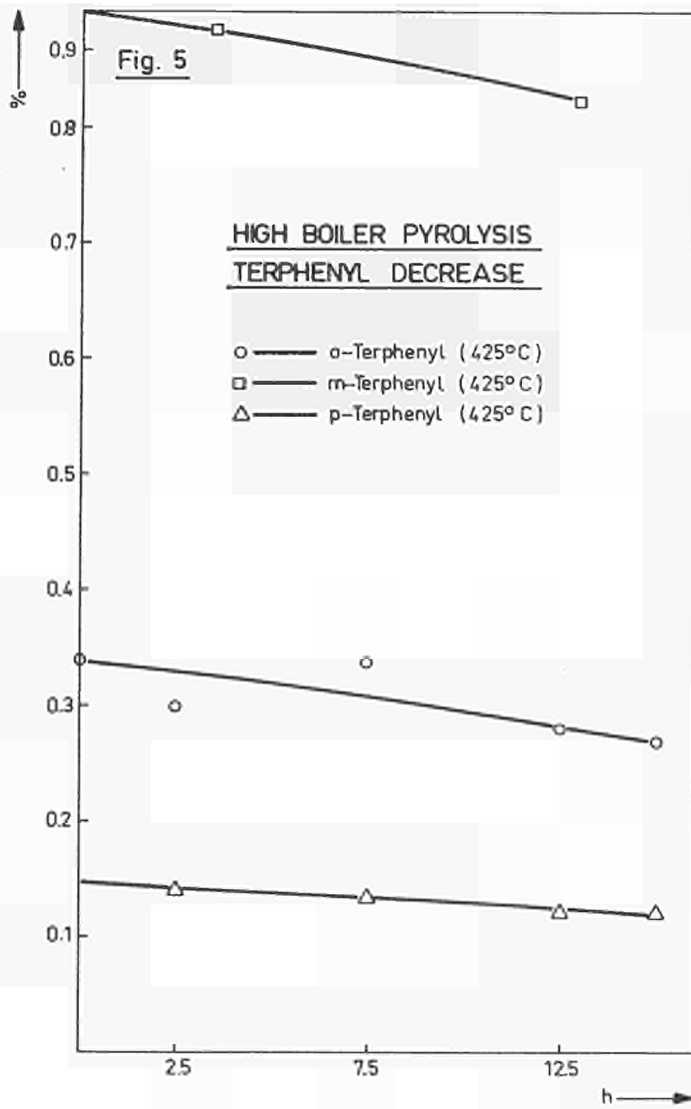
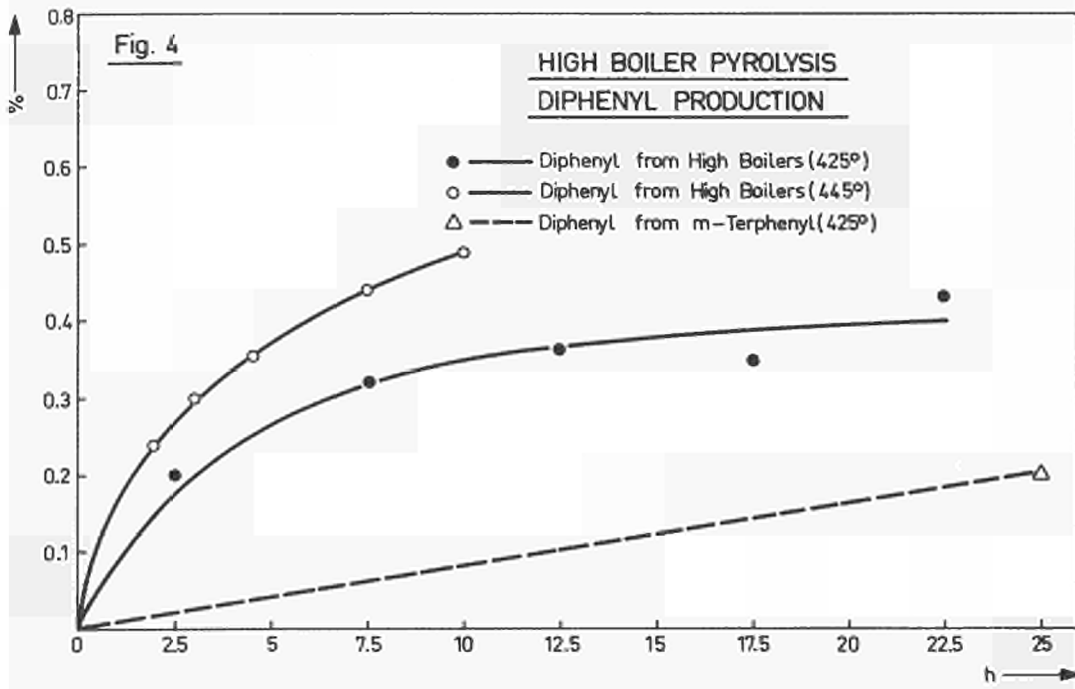
i) The gas obtained from the high boiler pyrolysis contains much more saturated and unsaturated hydrocarbons and less hydrogen than the gas resulting from the terphenyl pyrolysis indicating hydrogenated and alkylated components in the starting highboiling residue.

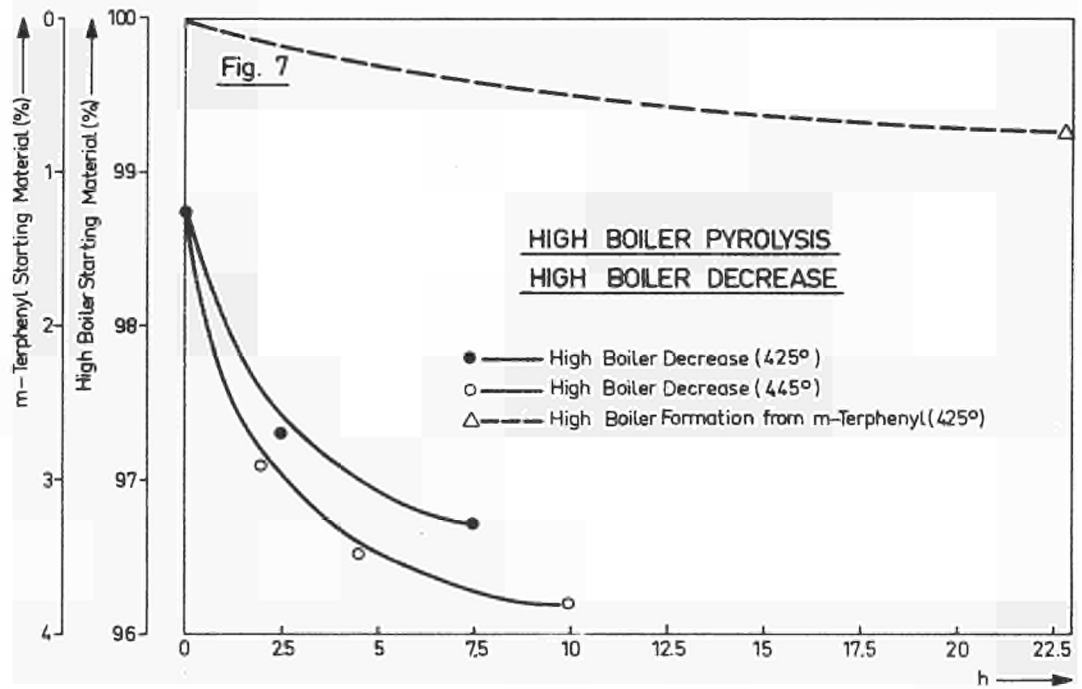
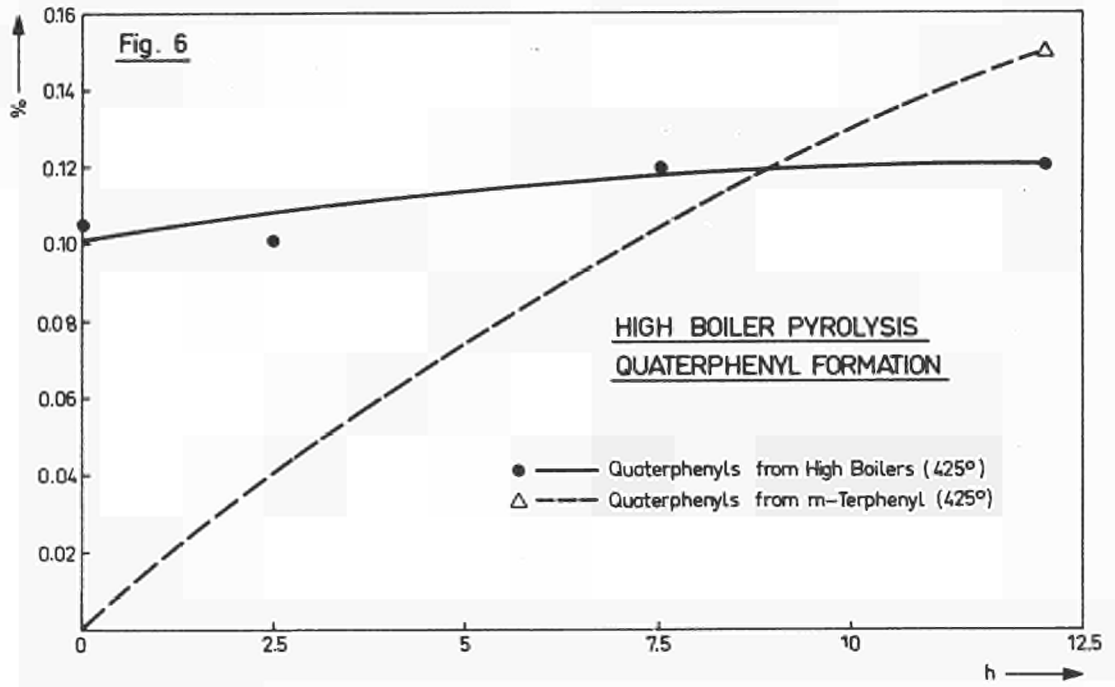
6 - A C K N O W L E D G E M E N T

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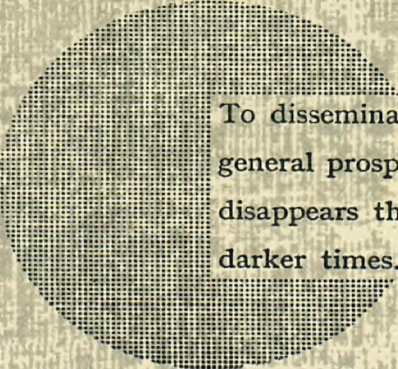
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To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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