

Determination of Hydrocarbon Constituents in the Benzene Pre-run

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The composition of the benzene pre-run has been investigated, mainly by gas chromatographic methods. Besides the main constituents carbon disulphide and benzene, it contains a large number of saturated and unsaturated hydrocarbons. Thus, it has been possible to identify 25 saturated and 35 unsaturated hydrocarbons in this part of the light oil.

For several years the volatile products obtained from the destructive distillation of coal have been the object of a number of investigations at this laboratory (*cf.* Ref. ¹). This work was started already in the early fifties but the separation methods available at that time made analytical investigations of complicated mixtures of hydrocarbons rather time-consuming and inexact. In recent years, however, new methods have been developed which render possible a successful solution of difficult separation problems concerning volatile hydrocarbons. Among these methods gas chromatography occupies a dominating position.

The present work, the first report of which was given in a lecture at the Scandinavian Chemists' 9th meeting at Aarhus, Denmark, in 1956, deals with a low-boiling fraction of the light oil, the benzene pre-run, sometimes also named the "crude carbon disulphide." It was the purpose of the investigation to determine the composition of the hydrocarbon part of this product in more detail than had previously been possible. The main constituents of the benzene pre-run are benzene, carbon disulphide and saturated and unsaturated hydrocarbons. In addition amines, mercaptans, hydrocyanic acid and neutral compounds of various kinds are also present.

Isolation of the hydrocarbon part of the benzene pre-run. To simplify the determination of the hydrocarbons, the non-hydrocarbon constituents were removed by first treating the benzene pre-run with 10 % sulphuric acid and 10 % ethanolic potassium hydroxide (*cf.* Fig. 1). The treatment was made using ice-cooling in order to reduce the losses of low-boiling hydrocarbons. In this way, the basic and acid parts were removed as well as the water-soluble neutral compounds, *e.g.* methanol, ethanol, acetaldehyde, acetone, acetonitrile

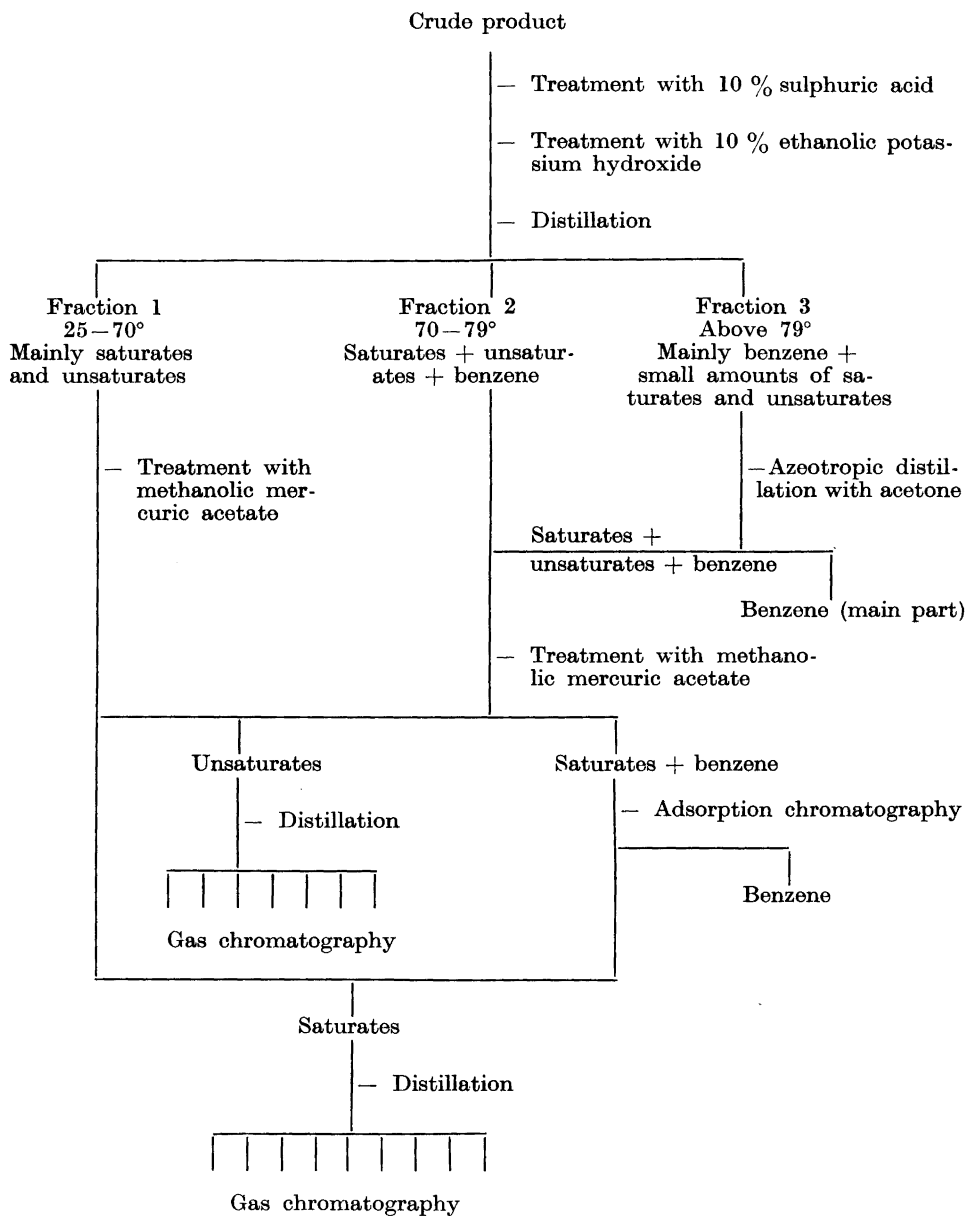


Fig. 1. Separation scheme for the benzene pre-run.

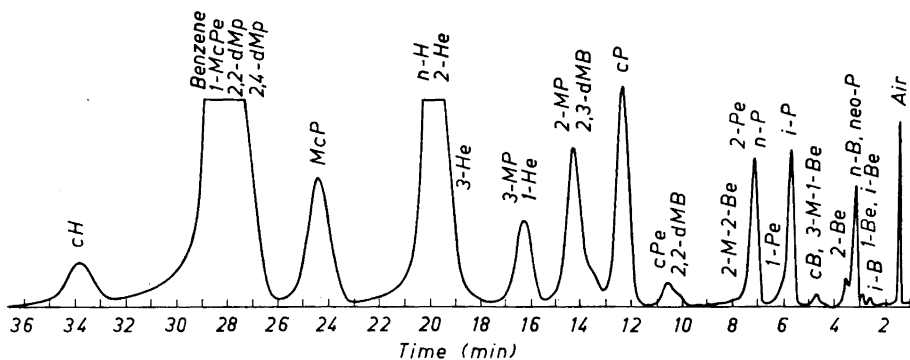


Fig. 2. Separation of the hydrocarbon part of the benzene pre-run. Column: tetraamylsilane (3%), 6 m. Temperature 25°C, flow of He 80 ml/min. Recorder attenuation 1/16, except for the ranges 2–3 min and 4–5 min (1/2), 3–4 min (1/4) and 6.5–8 min (1/64).

and methylisocyanide. The removal of carbon disulphide was based on the formation of potassium xanthogenate. It was found that a twofold treatment was necessary to remove all of the carbon disulphide present.

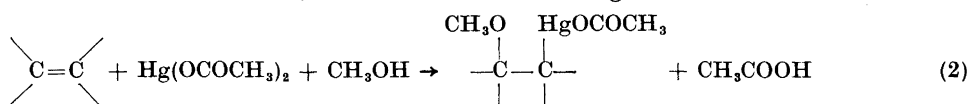
Removal of the main part of the benzene. The liquid left after the above treatment contained only traces of non-hydrocarbon constituents as shown by the sum of the percentages of carbon and hydrogen. * It was divided by distillation into three fractions boiling (1) between 25° and 70°, (2) between 70° and 79° and (3) above 79°. Fraction 1 was nearly free from benzene, fraction 2 was a mixture of benzene and saturated and unsaturated hydrocarbons and the main part of fraction 3 was benzene. To isolate the small amount (about 2%) of saturated and unsaturated hydrocarbons in fraction 3, the mixture was distilled with acetone. Benzene does not form an azeotrope with acetone while, however, this is generally the case with other hydrocarbons in this boiling range (*cf.* Ref. ²).

Separation of the saturated and unsaturated hydrocarbons. The mixture of hydrocarbons thus obtained is still too complex to be analyzed successfully by gas chromatographic methods. A necessary requirement is a preliminary separation of the unsaturated hydrocarbons from the saturated ones. After a survey of methods available for this purpose, it was decided to test two of them on the present mixture. In the first, adsorption chromatography on silica gel was utilized. It has been shown by Rossini *et al.*³ that selected mixtures of aromatic, olefinic and saturated hydrocarbons containing a small number of components may be separated according to type by displacement of the mixture from a silica gel column using methanol as a displacer. This method has also been developed into a valuable analytical tool for the determination of saturates, olefins and aromatics in hydrocarbon mixtures (*cf.* "The fluorescent indicator adsorption (FIA) method" by Criddle and LeTourneau⁴). Our

* A chromatogram, showing the gas chromatographic separation of this product using a tetraamylsilane column, is given in Fig. 2.

attempts to use this adsorption method on a larger scale for the separation of the present hydrocarbon mixture according to type were, however, not successful. The reason for this is probably the complexity of the unsaturated portion and the relatively low content of it in the mixture. It has been shown that the separation factor is dependent on the ratio between the components to be separated and that it decreases when the percentage of the major component increases, thus making it more difficult to get a good separation³.

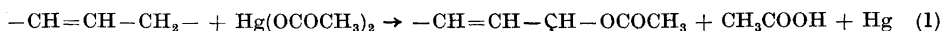
The second method selected for testing (and also finally chosen) involved the addition of the unsaturated hydrocarbons to mercuric acetate in the presence of methanol. This method, which is believed to be one of the mildest chemical ones available, is based on the following reaction: *



When treated with hydrochloric acid, the addition compound decomposes and the alkene is set free. The addition product is here formulated as a covalent methoxyacetoxymercurialkane. The question as to the real structure of the addition compound has, however, not received a definite answer yet. There are researchers in this field who consider the addition compound to be a more loosely bound molecular complex. ** The nature of the adduct is not only of theoretical but also of practical interest since this question is connected with the fate of geometrical isomers on addition to methanolic mercuric acetate. It has been stated by Spengler *et al.*⁶ that no isomerization of *cis-trans* isomers occurs when they are isolated from a mixture *via* their methoxyacetoxymercuric derivatives and then set free by acid. Brook and Wright⁷ on the other hand consider that an isomerization takes place although they report one case where a *cis* isomer could be isolated in a pure state.

Since the benzene pre-run is known to contain alkynes, their reaction with methanolic mercuric acetate is also of importance. It has been shown by Borisov *et al.*⁸ that mercuric acetate in acetic acid adds on to 2-butyne with the formation of 2-acetoxy-3-acetoxymercuri-2-butene which, with hydrochloric acid, yields methyl ethyl ketone. A method for the determination of C₄ and C₅ alkynes has been reported by Wagner *et al.*⁹ involving reaction of the alkynes in question with methanol in the presence of a mercuric oxide-boron trifluoride catalyst to form dimethyl ketals which are subsequently hydrolyzed to ketones. It was also found that 1,2-alkadienes were transformed to a great extent into ketones in the last-mentioned method, probably on account of a rearrangement to alkynes. From this, the conclusion can be drawn that there is a possibility that the alkynes and 1,2-alkadienes present in the benzene pre-run will be transformed into ketones on treatment with methanolic

* With cyclic olefins, mercuric acetate may react in another way at 130–150°.



Thus, mercuric acetate is not added to the double bond but a combined oxidation and acetylation occurs at a carbon atom adjacent to the C=C group⁵. However, this reaction does not take place under the conditions used in our experiments.

** For a discussion of this subject, *cf.* Ref.⁵

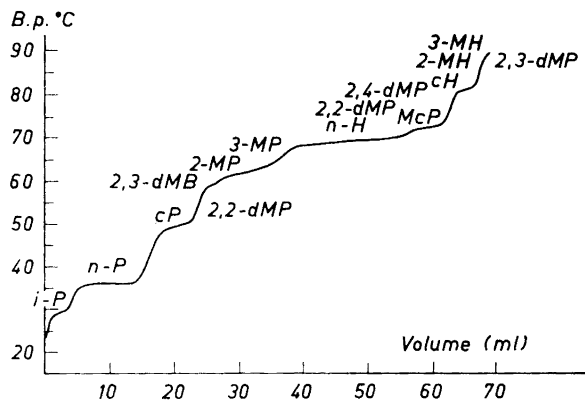


Fig. 3. Distillation curve of the saturated part of the benzene pre-run.

mercuric acetate followed by hydrolysis. Because of the aqueous solubility of many ketones in the actual range, they will be removed by the water (*cf.* the experimental part) and will not appear together with the hydrocarbons.

The practical performance of the methanolic mercuric acetate method has been worked out mainly by German researchers.¹⁰⁻¹³ It involves addition at room temperature, neutralization of the acetic acid formed and transformation of the methoxyacetoxymercuri derivatives into the corresponding chloroacetoxymercuri derivatives by shaking the reaction mixture with a solution of sodium chloride. The reason for the last-mentioned operation is that the chloro compound is considerably less soluble than the methoxy compound, on which account it precipitates and can be filtered from the solution. It is decomposed by means of hydrochloric acid and the olefins are distilled from the mixture with steam.

When this procedure was applied to the benzene pre-run, it was found that only a minor portion of the chloroacetoxymercuri addition compounds formed was precipitated, probably because of the low content of olefins in the mixture. This fact necessitated a modification of the separation procedure. Instead of transforming the methoxy derivative into the chloro derivative, the saturated hydrocarbons were separated from the original addition product by steam distillation. The residual addition compound was then decomposed by acid and the mixture steam distilled again to separate the olefins. When this technique was applied to mixtures of known composition, a satisfactory separation was obtained in one run. This was also the case with the fractions from the benzene pre-run as shown by the bromine number of the saturated portion after the separation.

The saturated part from fractions 2 and 3 (*cf.* Fig. 1) still contained some benzene which was separated by adsorption chromatography on silica gel. All of the saturated parts from the benzene pre-run were then united and distilled using an efficient column. The unsaturated parts were treated in the same way. The results of the distillations are shown in Figs. 3 and 4.

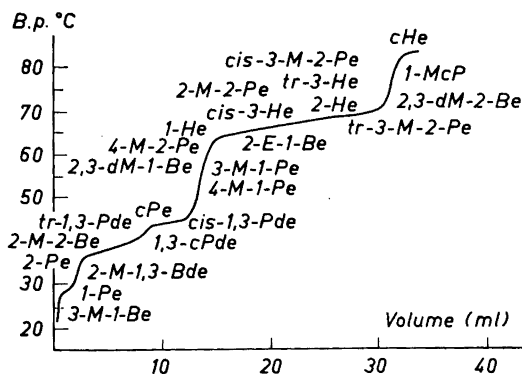


Fig. 4. Distillation curve of the unsaturated part of the benzene pre-run.

Gas chromatographic investigation. The compositions of the fractions obtained on distillation were investigated by gas chromatographic methods. Due to the preliminary distillation, the analysis was considerably simplified. In the gas chromatographic investigation, each fraction from the distillation was analyzed separately and the percentages of the various compounds detected were then added to give the total percentages of the compounds in question in the hydrocarbon part of the benzene pre-run. This method is somewhat lengthy and hardly suited as a regular analytical method for this product. However, it was not our aim to develop such a method but to try to get as detailed a picture as possible of the composition of the hydrocarbon part of the benzene pre-run. The procedure used in the gas chromatographic investigation was mainly the following.

A. *The saturated part.* (1) The boiling point of the components and their hydrocarbon type were established. For this purpose two stationary phases, namely tetraamylsilane (TAS) and dimethylsulpholane (DMS), were utilized. The boiling point was calculated from the relative retention time on TAS and the hydrocarbon type obtained by putting the relative retention times on TAS and DMS into a retention diagram. The procedure involved has been described elsewhere (*cf.* Ref. ¹⁴).

(2) Each fraction was further scanned using a number of packed columns containing various stationary phases, namely dioctyl phthalate (DOP), butylsulphidacetic acid (BSA), β, β' -oxydipropionitrile (ODP) and silver nitrate/ethylene glycol (AgEG). The last stationary phase was mainly used for the detection of remaining traces of unsaturated hydrocarbons. A description of the application of these stationary phases as well as the relative retention times on them of a large number of hydrocarbons in the actual boiling range has been given previously (*cf.* Refs. ^{14,15}). A capillary column coated with squalane was also utilized at a later stage of this work.

(3) With a knowledge of the type and boiling point of a hydrocarbon and of its relative retention time on a number of columns, a fairly certain identification of it could be arrived at. In rare cases it was necessary to freeze out a

Table 1. Saturated hydrocarbons found in the benzene pre-run.

Hydrocarbon	Boiling point * °C	Wt. % of the saturated hydrocarbons **	Wt. % of the benzene pre-run
Alkanes			
Isobutane	-11.7	Trace ***	Trace
Butane	-0.5	0.14	0.05
Neopentane	9.5	Trace	Trace
Isopentane	27.9	3.8	1.2
Pentane	36.1	17.1	5.4
2,2-Dimethylbutane	49.7	0.41	0.13
2,3-Dimethylbutane	58.0	1.6	0.51
2-Methylpentane	60.3	9.5	3.0
3-Methylpentane	63.3	4.7	1.5
Hexane	68.7	30.6	9.7
2,2-Dimethylpentane	79.2	0.30	0.10
2,4-Dimethylpentane	80.5	0.50	0.16
2,2,3-Trimethylbutane	80.9	0.04	0.01
3,3-Dimethylpentane	86.1	0.04	0.01
2,3-Dimethylpentane	89.8	0.54	0.17
2-Methylhexane	90.1	0.46	0.15
3-Methylhexane	91.9	0.25	0.08
3-Ethylpentane	93.5	0.09	0.03
Heptane	98.4	0.01	Trace
Cycloalkanes			
Cyclobutane	12.5	Trace	Trace
Methylocyclobutane	36.3	0.31	0.10
Cyclopentane	49.3	9.4	3.0
Methylocyclopentane	71.8	11.2	3.6
Cyclohexane	80.7	3.9	1.2
Methylocyclohexane	100.9	Trace	Trace

* According to Ref.²⁶

** Calculated on the charge before distillation (31.8 wt.% of the benzene pre-run). The distillation losses amounted to 5.1 %.

*** Less than 0.005 %.

fraction responsible for a peak in a chromatogram and to examine it by infrared spectroscopy. By means of these methods a rather detailed picture of the composition of the various fractions of the saturated hydrocarbon part of the benzene pre-run could be obtained.

(4) The quantitative analysis was based on the internal normalization method in which the per cent area under the peaks is put equal to the weight per cent. This method is afflicted with certain errors but it has been deemed unnecessary to increase the accuracy by calibration since the inherent errors due to losses in the various separation procedures to which the product was subjected before the gas chromatographic analysis are rather great. The fact that the hydrocarbons analyzed in each fraction from the distillation are not very dissimilar in molecular size also tends to reduce the errors.

Table 2. Unsaturated hydrocarbons found in the benzene pre-run.

Hydrocarbon	Boiling point * °C	Wt. % of the unsaturated hydrocarbons **	Wt. % of the benzene pre-run
Alkenes			
Propene	-47.7	Trace***	Trace
Isobutene	-6.9	Trace	Trace
1-Butene	-6.3	Trace	Trace
<i>trans</i> -2-Butene	0.9	0.13	Trace
<i>cis</i> -2-Butene	3.7	0.17	Trace
3-Methyl-1-butene	20.1	0.22	0.01
1-Pentene	30.0	3.1	0.08
2-Methyl-1-butene	31.2	0.12	Trace
<i>trans</i> -2-Pentene	36.4	11.5	0.31
<i>cis</i> -2-Pentene	36.9	5.7	0.15
2-Methyl-2-butene	38.6	2.8	0.08
4-Methyl-1-pentene	53.9	1.0	0.03
3-Methyl-1-pentene	54.1	1.0	0.03
2,3-Dimethyl-1-butene	55.7	0.24	0.01
<i>cis</i> -4-Methyl-2-pentene	56.3	0.47	0.01
<i>trans</i> -4-Methyl-2-pentene	58.6	0.14	Trace
2-Methyl-1-pentene	60.7	0.02	Trace
1-Hexene	63.5	14.0	0.38
2-Ethyl-1-butene	64.7	0.42	0.01
<i>cis</i> -3-Hexene	66.4	2.4	0.06
2-Methyl-2-pentene	67.3	0.48	0.01
<i>cis</i> -3-Methyl-2-pentene	67.6	0.23	0.01
<i>trans</i> -3-Hexene	67.9	5.8	0.16
<i>trans</i> -2-Hexene	67.9	19.5	0.53
<i>cis</i> -2-Hexene	68.8	7.1	0.19
<i>trans</i> -3-Methyl-2-pentene	70.5	1.4	0.04
2,3-Dimethyl-2-butene	73.2	0.11	Trace
Alkadienes			
2-Methyl-1,3-butadiene	34.1	0.48	0.01
3-Methyl-1,2-butadiene	40	0.05	Trace
<i>trans</i> -1,3-Pentadiene	42.0	0.71	0.02
<i>cis</i> -1,3-Pentadiene	44.1	0.27	0.01
Cycloalkenes			
Cyclopentene	44.2	11.2	0.32
1-Methylcyclopentene	75.8	0.17	Trace
Cyclohexene	83.0	3.1	0.08
Cycloalkadienes			
1,3-Cyclopentadiene	42.5	1.2	0.03

* According to Ref.²⁶

** Calculated on the charge before distillation (2.7 wt. % of the benzene pre-run). The distillation losses amounted to 4.5 %.

*** Less than 0.005 %.

B. *The unsaturated part.* (1) The boiling point and hydrocarbon type were determined in the same way as for the saturated hydrocarbons. In this case, however, it is not always sufficient to run the compound on TAS and DMS

to get the hydrocarbon type since sometimes a hydrogenation procedure must also be applied (*cf.* Refs. ^{14,16}).

(2) The stationary phases mentioned above and those already given under A, 2, were utilized for the separation of each fraction from the distillation into as many components as possible.

(3) In addition to the qualitative hydrogenation procedure referred to under B, 1, a method for the quantitative hydrogenation of fractions isolated from analytical gas chromatographs was sometimes utilized to settle the structure of an olefin. ¹⁷ Ozone oxidation was also employed in some cases in order to investigate the occurrence of certain types of olefins in a fraction, preferably α -alkenes. ¹⁸

(4) For the quantitative analysis, the internal normalization method was used as in the case of the saturated hydrocarbons (*cf.* A, 4).

The composition of the hydrocarbon part of the benzene pre-run. In Tables 1 and 2, the saturated and unsaturated hydrocarbons found in the hydrocarbon part of the benzene pre-run have been tabulated. Their weight percentages, calculated on the saturated and unsaturated parts, respectively, and on the total benzene pre-run, are also given. These values must be considered to be rather approximate in view of the losses occurring in the various separation procedures. Naturally, the losses of low-boiling compounds were largest, and it is also seen that C₁ and C₂ hydrocarbons are absent.

The proportion between the *cis* and *trans* isomers of olefins given in Table 2 is not necessarily that prevailing in the original product because of the possibility of a *cis-trans* isomerization taking place upon treatment of these compounds with the methanolic mercuric acetate (*cf.* p. 286). The total absence of alkynes and the low content of 1,2-alkadienes is noteworthy but not unexpected considering the reported mode of reaction of these hydrocarbons with mercuric acetate and similar reagents (*cf.* p. 286). Obviously methanolic mercuric acetate is an unsuitable reagent for the separation of these types of unsaturated hydrocarbons. Other methods for separating them from the rest of the benzene pre-run are now under investigation. The amount of cyclopentadiene found is low, probably due to the fact that the benzene pre-run investigated had been stored for some time and that cyclopentadiene tends to polymerize during storage.

Since this work was completed Stavinoha and Nash ¹⁹ have reported an investigation of the impurities in acid-washed 1° coke-oven benzene using gas chromatography and mass spectrometry. Of the 16 identified saturated hydrocarbons, 11 have been found also in the benzene pre-run while 4 dimethylcyclopentanes and one trimethylcyclopentane have not been encountered here. This does not necessarily mean that they were absent. Their concentrations in the coke-oven benzene are of the order of 0.01 % and should be even lower in the benzene pre-run. Further, analyses in the hydrocarbon range in question using gas chromatography alone are not quite reliable because of the difficulty of achieving complete separation. On this account, a combination of gas chromatography and mass spectrometry is generally used in this hydrocarbon range.

It is seen from Table 1 that the major part of the saturates and unsaturates consists of a relatively small number of hydrocarbons. Thus, 90 % of the saturated part was composed of 8 of the 25 compounds found, namely isopen-

tane (3.8 %), pentane (17.1 %), 2-methylpentane (9.5 %), 3-methylpentane (4.7 %), hexane (30.6 %), cyclopentane (9.4 %), methylcyclopentane (11.2 %) and cyclohexane (3.9 %). In the same way, 90 % of the unsaturated part was made up of 8 of the 29 compounds identified *, namely 1-pentene (3.3 %), 2-pentene (18.1 %), 2-methyl-2-butene (2.9 %), 1-hexene (14.7 %), 2-hexene (28.2 %), 3-hexene (8.6 %), cyclopentene (11.8 %) and cyclohexene (3.3 %). As might be expected, the carbon skeletons of the most common saturated and unsaturated hydrocarbons are on the whole the same. The dominant position of the straight chain C_5 and C_6 hydrocarbons is clearly shown. They constitute about 50 % of the saturated and about 75 % of the unsaturated part. It must, however, be kept in mind that a part of the lower hydrocarbons has presumably been lost during the separation procedures.

The routine analysis of the benzene pre-run. It has been pointed out previously that the investigation method followed in this work is less suited for the routine analysis of the benzene pre-run. In fact, the composition of this product is so complex that a complete analysis can hardly be achieved by any simplified method; one has always to make a certain sacrifice in accuracy in order to speed up the analysis. However, in many cases, information concerning the main constituents should suffice. For this purpose gas chromatographic methods have been applied.

Janák and Vojtovič²⁰ have chromatographed the crude benzene pre-run and obtained 21 chromatographic fractions that could be quantitatively assessed. It is, however, obvious that any detailed analysis cannot be obtained in this way. Values are given for benzene, carbon disulphide, some mercaptans and for 9 saturated and 7 unsaturated hydrocarbons. Since no separation of the pentenes in the 30–31° and 36–39° ranges or of the hexenes in the 61–69° range is achieved a composite value for each of these fractions is obtained. It is noteworthy that some of the hydrocarbons, found in the present work to belong to the main constituents, are absent, *e.g.* 3-methylpentane, cyclopentane, cyclopentene and cyclohexene. In spite of these shortcomings the Janák-method may, however, be of practical value.

To investigate the usefulness of a capillary column for the routine analysis of the hydrocarbon part of the benzene pre-run the liquid left after the treatment with sulphuric acid and ethanolic potassium hydroxide was run on a 150 feet capillary column coated with squalane. There were obtained about 30 resolved peaks which furnish a good base for an analysis, especially of the saturated portion. The informations obtained about the unsaturated part were not so detailed. However, preliminary experiments carried out in this laboratory indicate that a separation of the saturated and unsaturated portions of the hydrocarbons in the benzene pre-run, good enough for the purpose, might be achieved using a silver nitrate/ethylene glycol packed column. The condensed saturated and unsaturated parts could then be further analyzed using the capillary column.

The interpretation of the chromatograms from the capillary column has to be built on the investigations previously described in this work. Without a knowledge of the main part of the constituents present in the mixture the

* *Cis* and *trans* isomers of the same hydrocarbon counted as one compound.

identification of the compounds in the chromatogram would be rather uncertain since it would be based solely on a comparison of relative retention times on this only column. This is due to the fact that no fractions can be frozen out for further investigations. With the application of capillary columns containing other stationary phases the identification situation, however, could be improved. We believe that in the future capillary columns with their great separation efficiency will come to play an important rôle in the analysis of complicated mixtures of hydrocarbons, such as that studied in this work.

EXPERIMENTAL

The benzene pre-run investigated was obtained from the Gas Works of Gothenburg. It was isolated by distillation up to a temperature of 79° and its content of carbon disulphide was 9.4 % according to analysis (*cf.* below).

Treatment with sulphuric acid. The benzene pre-run was mixed with 20 % by volume of 10 % sulphuric acid in a round bottomed flask equipped with stirrer and double reflux condensers. The mixture was cooled in ice water and then rapidly stirred for 15 min. In order to minimize losses by evaporation, ice water was passed through the condensers. The acid was siphoned from the flask and the hydrocarbon layer washed with cold water. The decrease in weight of the benzene pre-run amounted to 3.0 %.

Treatment with ethanolic potassium hydroxide. To the contents in the flask, an equal volume of a cold 10 % solution of potassium hydroxide in 90 % ethanol was added. The mixture was rapidly stirred under cooling for 30 min. The alkaline solution was siphoned from the flask and the treatment repeated, this time with half as much ethanolic potassium hydroxide as before. After withdrawal of the lower layer, the residual hydrocarbon layer was washed with cold water and dried over anhydrous calcium sulphate. The decrease in weight amounted to 10.0 %.

Distillation of the purified benzene pre-run. The benzene pre-run which had now been freed from the majority of the non-hydrocarbon constituents was divided by distillation * into three fractions boiling (1) between 25 and 70°, (2) between 70 and 79° and (3) above 79°. Fraction 1 (38 % by weight of the distillate) had $n_D^{20} = 1.388$, H + C = 99.8 %, H:C = 2.10 and bromine number = 20.5. Fraction 2 (15 %) had $n_D^{20} = 1.458$, H + C = 99.7 %, H:C = 1.36 and bromine number = 5.0. Fraction 3 (47 %) had $n_D^{20} = 1.496$, H + C = 100.2 %, H:C = 1.08 and bromine number = 0.7.

Azeotropic distillation of fraction 3 with acetone. Fraction 3 was mixed with 20 % by volume of acetone and the mixture distilled in the apparatus described in the previous section. One fraction was taken between 5° and 56° and a second between 56° and 79°. The acetone was removed by washing the fractions with cold water. After drying over anhydrous calcium sulphate, there was obtained from the first fraction a product amounting to 2.2 % of fraction 3 and with $n_D^{20} = 1.412$. The second fraction yielded a product amounting to 3.4 % of fraction 3 and with $n_D^{20} = 1.493$. The main part of this fraction is benzene. The residual benzene left after the azeotropic distillation constituted 92.3 % of fraction 3 and had $n_D^{20} = 1.499$. Since pure benzene has $n_D^{20} = 1.501$, it appears that only very small amounts of saturated and unsaturated hydrocarbons are left in the benzene.

Treatment with methanolic mercuric acetate. To isolate the unsaturated part of the hydrocarbons, a portion of the mixture was shaken in a sealed bottle for 3 h at room temperature with an equal volume of a methanol solution of mercuric acetate containing 2 to 3 times the theoretically necessary amount of mercuric acetate.** It was found that the addition reaction was promoted if the mercuric acetate was dried before use.

* A 90 × 2.5 cm column, packed with glass helices and equipped with an automatic still head timer and a dual heating unit for the column, which permitted its operation under essentially adiabatic conditions, was used. (Manufactured by Todd Scientific Co., Springfield, Pa, USA, See also Ref.²¹).

** Calculated on the basis of the bromine number.

The reaction mixture was cooled in ice water and then transferred to a distillation flask where it was neutralized with dilute sodium hydroxide in some excess and then steam distilled. To decrease the evaporation losses, two long condensers through which ice water was passed were used and, in addition, the receiver was cooled in ice water. The hydrocarbons on to which mercuric acetate had not been added were separated in this way. The hydrocarbon layer in the receiver was washed with ice water to remove methanol and dried over anhydrous calcium sulphate.

The residue in the distillation flask was made distinctly acidic using dilute hydrochloric acid and then steam distilled, taking the same precautions to prevent evaporation losses as before. The layer of unsaturated hydrocarbons collected in the receiver was washed with ice water and dried over anhydrous calcium sulphate.

Fraction 2 from the regular distillation was combined with the two fractions isolated by the azeotropic distillation of fraction 3 and treated with methanolic mercuric acetate as described above. There were obtained an unsaturated fraction * (2.1 %) with $n_D^{20} = 1.399$ and bromine number = 173 and a saturated and aromatic fraction (95.6 %) with $n_D^{20} = 1.463$ and bromine number = 0.

When fraction 1 from the regular distillation was treated with methanolic mercuric acetate, there resulted an unsaturated fraction (7.9 %) with $n_D^{20} = 1.388$ and bromine number = 200 and a saturated fraction (86.2 %) with $n_D^{20} = 1.381$ and bromine number = 0.6.

Separation of saturates from benzene by adsorption chromatography. The saturated part obtained in the first mercuric acetate separation in the previous section contained a considerable amount of benzene. It was considered advisable to remove this by adsorption chromatography on silica gel since it might interfere in the gas chromatographic investigation.

The adsorption column used consisted of a jacketed glass tube, 1.5 m long. The upper 0.75 m of the tube had an internal diameter of 25 mm while, for the remainder of the tube, the diameter was 10 mm. A sintered glass plate of medium porosity was placed at the bottom of the tube. The lower end of the column had a stopcock and the ends of the tube were equipped with ground joints. A graduated receiver was attached to the lower end and a reservoir with a stopcock to the upper end.

An experiment was performed in the following way. The column was filled with about 300 g of 100–200 mesh silica gel. The mixture to be separated (about 40 ml) was poured into the reservoir and permitted to flow into the silica gel layer. Additional silica gel (about 7 cm) was then added to the column. The reservoir was filled with the desorbent (methanol) and a pressure of 100 mm Hg applied. Ice water was passed through the jacket and the receiver was likewise cooled. The flow of liquid from the column was maintained at 5 to 10 ml/h and fractions of 0.5 to 2 ml were taken and their refractive indices measured. The separation obtained was found to be good, the intermediate fractions between saturates and benzene amounting to less than 10 % of the total charge. In this way the saturated part, about 40 % of the mixture of saturates and benzene, was separated. Its refractive index was $n_D^{20} = 1.401$.

Distillation of the saturated and unsaturated parts. The saturated fractions obtained in the previous separation (31.8 % of the benzene pre-run) were united and fractionated in the same distillation apparatus that was previously used in this work (*cf.* p. 293). However, the column in this case consisted of a 90×0.5 cm glass tube containing a monel spiral with a core rod. The number of theoretical plates obtained at total reflux was about 60. The distillation curve for the saturated part is given in Fig. 3.

The unsaturated fractions, amounting to 2.7 % of the benzene pre-run, were united and fractionated in the same still. The distillation curve is given in Fig. 4. The constituents in the various saturated and unsaturated fractions were then subjected to separation by gas chromatography.

Gas chromatographic investigation. Perkin-Elmer Vapour Fractometers, Models 154 and 116 E, were used. The preparation of the packed columns utilized has been described and their data have been given elsewhere (*cf.* Refs. ^{14,15,23}). The capillary column used consisted of a 150 feet \times 0.010 inch (inside diameter) Perkin-Elmer Golay column U,

* This fraction also contained some thiophene which has been shown to react with mercuric acetate with the replacement of hydrogen atoms by acetoxymercuri groups ²².

coated with squalane. The capillary column was used in conjunction with a Perkin-Elmer hydrogen flame ionization detector. In other cases a thermistor detector was utilized.

Analysis methods. Carbon disulphide was determined mainly according to Matuszak²⁴. The sample (0.1–0.3 g) was weighed in a sealed thin-walled glass ampoule which was put in a 50 ml Erlenmeyer flask containing 2 ml 10 % absolute ethanolic potassium hydroxide. The glass ampoule was broken beneath the surface of the caustic and 1 N acetic acid slowly added until the solution was just acid to phenolphthalein. Starch indicator was added and the solution titrated to the starch blue end point with 0.1 N standard iodine solution. The analysis is based on the reaction.



Bromine number. The ASTM-method D 1158–55T was used. It involves the treatment of the sample dissolved in carbon tetrachloride, with an excess of bromide-bromate solution in the presence of glacial acetic acid. The excess bromine is reduced with potassium iodide and the liberated iodine determined by titration with sodium thiosulphate solution. For details cf. Ref.²⁵

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