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GAS CHROMATOGRAPHIC STUDY OF METHYLSTYRENES IN THE LIGHT-OIL FRACTION OF COAL DISTILLATE USING SELECTIVE HYDROGENATION

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SUMMARY

The catalytic hydrogenation of olefinic aromatic hydrocarbons, such as styrene, α - and β -methylstyrene, *o*-, *m*- and *p*-methylstyrenes and indene in the light-oil fraction was carried out by a selective method, the aromatic rings being kept intact. Gas chromatography was employed to identify the starting materials and the products.

The chromatograms of the hydrogenated and non-hydrogenated samples which were obtained under identical conditions were compared. The qualitative and quantitative determination of these compounds was based on the shifts of the peaks after the hydrogenation process, and calculation of the new peak areas (e.g., the shift from α -methylstyrene to cumene), and it was therefore possible to identify methylstyrenes in the light-oil fraction from their well separated peaks in the chromatograms.

INTRODUCTION

The oxygen bridges of heterogeneous rings in coal are broken down by pyrolysis¹, yielding various light compounds that can be measured by gas chromatography (GC)²⁻⁹. The light-oil fraction of coal distillate obtained from the pyrolysis of coal in coking plants is generally a mixture of mono- and dicyclic hydrocarbons¹⁻⁹. The optimum pyrolysis temperature of coal to produce the maximum yield of aromatic hydrocarbons is 700-900° (ref. 1), which is the same temperature range obtained for cleavage of phenolic (OH) bonds¹⁰ in the pyrolysis of phenoplast to increase the percentage of aromatic hydrocarbons.

Platinum^{11,12}, palladium^{11,13,14}, nickel¹⁵, copper^{15,16} and zinc¹⁷ have been used as catalysts for the hydrogenation process, and of these the copper catalyst prepared according to the Sabatier and Sanders method¹⁵ was used in this work, because it gave the best results in the selective hydrogenation of ethylenic and dienic double bonds, whereas the aromatic and heterogeneous rings remained unaffected. In this work, with some modifications applied to the methods of Beroza¹¹ and Thompson and co-workers^{18,19}, the catalytic hydrogenation process was carried out in the injector block.

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EXPERIMENTAL

Materials

Sample. The light-oil (crude benzole) fraction of coal distillate was obtained from the pyrolysis of coal at the Coking Plant in the Esfahan Steel Mill, Iran.

Standard solution of hydrocarbons. Hydrocarbons (laboratory-reagent grade), were purchased from Merck-Schuchardt (Darmstadt, G.F.R.). A mixture of thiophene (50 μ l), toluene (500 μ l), ethylbenzene (10 μ l), *p*-xylene (100 μ l), *m*-xylene (100 μ l), *o*-xylene (50 μ l), *n*-propylbenzene (5 μ l), mesitylene (5 μ l), 1,2,4-trimethylbenzene (5 μ l), 1,2,3-trimethylbenzene (5 μ l), cumene (1 μ l), *p*-ethyltoluene (5 μ l), *m*-ethyltoluene (5 μ l), *o*-ethyltoluene (5 μ l), styrene (5 μ l), α -methylstyrene (10 μ l), *m*- and *p*-methylstyrene (10 μ l; 60% *m*-), allylbenzene (5 μ l), coumarone (5 μ l), indene (50 μ l), tetrahydronaphthalene (50 μ l), naphthalene (50 mg), and dicyclopentadiene (15 μ l) was injected into a 5-ml vial containing 4 ml of benzene and kept in a cool location.

Other materials. Chromosorb P AW (60–80 mesh) was obtained from Varian Aerograph (Walnut Creek, Calif., U.S.A.).

To prepare copper hydroxide mixed with Chromosorb P, copper hydroxide was precipitated from a hot solution of copper sulphate by adding an excess of sodium hydroxide, the black precipitate was decanted three times and then transferred to a vacuum oven at 50°. The product contained 50% of copper after reduction.

Apparatus

A Varian Aerograph Model 2800 gas chromatograph equipped with a flame-ionization detector was used.

Operating conditions

A capillary column was used with hydrogen as carrier gas (flow-rate 1.35 ml/min), with an air flow-rate of 300 ml/min and a hydrogen flow-rate of 25 ml/min and an electrometer setting of $10^{-10} \times 1$, $10^{-11} \times 1$ A/mV. The stainless-steel capillary column (200 ft. \times 0.01 in. I.D.) was packed with poly(*m*-phenyl ether) (6-ring) and stabilized at 150° with nitrogen at a flow-rate of 1 ml/min for 48 h. The column temperature was maintained at 50° for 15 min, then programmed at two rates, first at 1°/min up to 110° and then at 4°/min up to 150°. The injector temperature was 240° and the detector temperature 240°. A 0.5-ml volume of the sample (or standard) was injected, the splitting ratio being 1:50.

An FFAP column was used with hydrogen as carrier gas (flow-rate 30 ml/min), with an air flow-rate of 300 ml/min and an electrometer setting of $10^{-9} \times 16$, $10^{-10} \times 16$ A/mV. A coiled copper column (24 ft. \times 1/8 in. I.D.) was packed with 15% FFAP on Chromosorb P and stabilized at 250° with nitrogen at a flow-rate of 15 ml/min for 24 h. The column temperature was programmed from 60° to 150° at a rate of 2°/min and then from 150° to 240° at a rate of 20°/min. The injector temperature was 240° and the detector temperature 240°. The injection volume was 0.5 μ l.

Hydrogenation unit

The injector block of the gas chromatograph was used as a hydrogenation unit. The injector tube (136.5 \times 3.2 mm I.D.) was packed with Chromosorb P (0.25 g), copper hydroxide mixed with Chromosorb P (0.15 g) and Chromosorb P (0.10 g).

The catalyst was activated at 400° by passing hydrogen through the tube at a rate of 50 ml/min for 1 h. In the non-hydrogenation process, the injector tube was packed with Chromosorb P alone (0.5 g).

RESULTS AND DISCUSSION

Throughout this section the numbers in parentheses refer to the corresponding peaks in the chromatograms.

The results are summarized in Table I.

TABLE I
CHEMICAL COMPOSITION OF THE LIGHT-OIL FRACTION

<i>Non-hydrogenatable compounds</i>			<i>Hydrogenatable compounds</i>		
<i>Name</i>	<i>Content</i> (%, w/w)	<i>Peak</i> <i>No.</i>	<i>Name</i>	<i>Content</i> (%, w/w)	<i>Peak</i> <i>No.</i>
Benzene	70.0	1	Styrene	1.2	9
Thiophene	0.045	2	Allylbenzene	—	13
Toluene	13.20	3	α -Methylstyrene	0.03	17
Ethylbenzene	0.09	4	<i>p</i> -Methylstyrene	0.11	} 18
<i>p</i> -Xylene	0.90	5	<i>m</i> -Methylstyrene	0.20	
<i>m</i> -Xylene	2.50	6	<i>o</i> -Methylstyrene	0.025	19
<i>o</i> -Xylene	0.45	7	β -Methylstyrene	0.018	—
Cumene	—	8	Dicyclopentadiene	0.35	26
<i>n</i> -Propylbenzene	0.003	10	Indene	0.95	23
<i>p</i> -Ethyltoluene	0.02	11			
<i>m</i> -Ethyltoluene	0.045	12			
Mesitylene	0.25	14			
<i>o</i> -Ethyltoluene	0.006	15			
1,2,4-Trimethylbenzene	0.28	16			
1,2,3-Trimethylbenzene	0.05	20			
Coumarone	0.048	21			
Indane	0.03	22			
Naphthalene	3.1	25			

By comparing the chromatograms of hydrogenated (Figs. 1, 2 and 5) and non-hydrogenated (Figs. 3, 4 and 6) standard solutions and light oil obtained under identical conditions, it was found that after hydrogenation the peaks of styrene (9), allylbenzene (13), α -methylstyrene (17), *m*- and *p*-methylstyrene (18), *o*-methylstyrene (19) and indene (23) had disappeared and shifted to the corresponding hydrogenated forms as follows: ethylbenzene (4), *n*-propylbenzene (10), cumene (8), *m*-ethyltoluene (12), *p*-ethyltoluene (11), *o*-ethyltoluene (15) and indane (22), respectively. Dicyclopentadiene (26) was only decomposed by the hydrogenation and the main peak (27) identified.

When an FFAP column was used the peaks of styrene, dicyclopentadiene and an unknown compound (U) overlapped (Fig. 6). The styrene peak was shifted to ethylbenzene (4) by the hydrogenation process (Fig. 5), and also the peak of α -methylstyrene had been eliminated, the hydrogenated form of dicyclopentadiene (27) appeared in place of (17), and the unknown compound remained unaffected (Fig. 5).

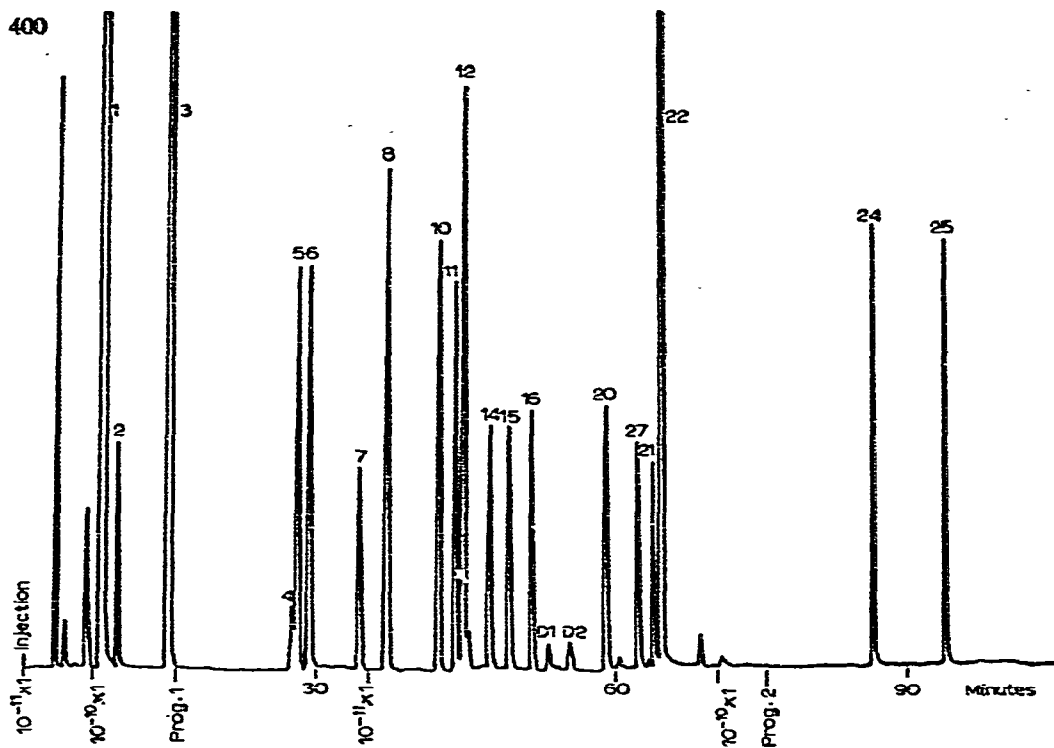


Fig. 1. Chromatogram of standard hydrocarbons using copper catalyst for hydrogenation and a capillary column.

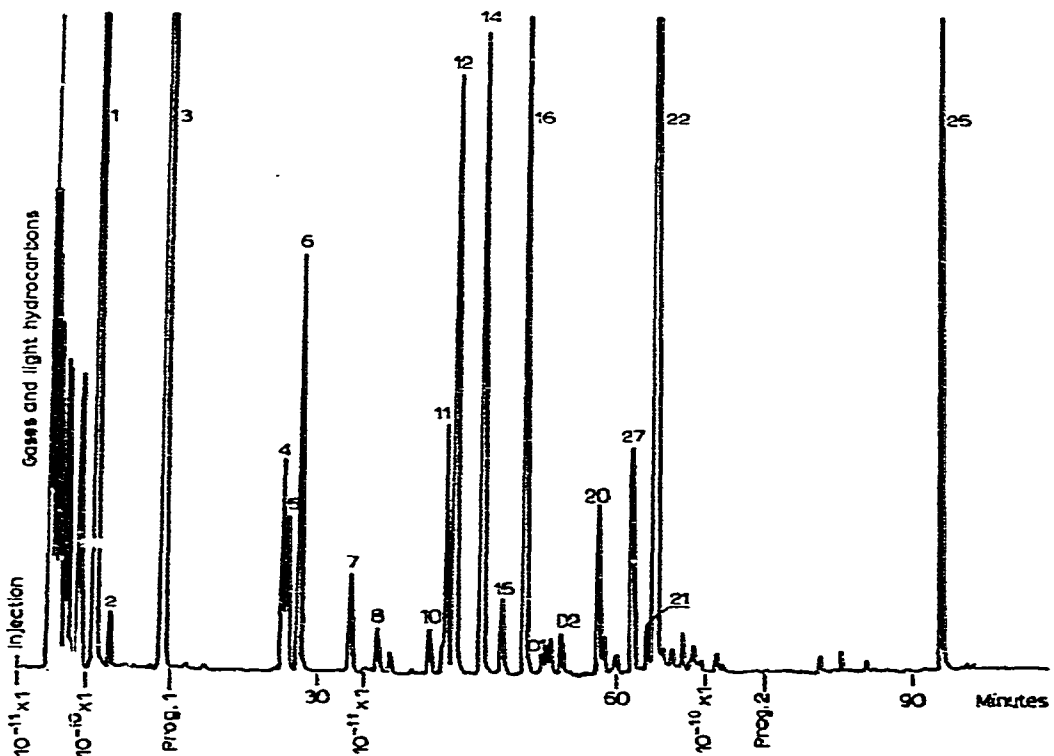


Fig. 2. Chromatogram of light oil using a copper catalyst for hydrogenation and a capillary column.

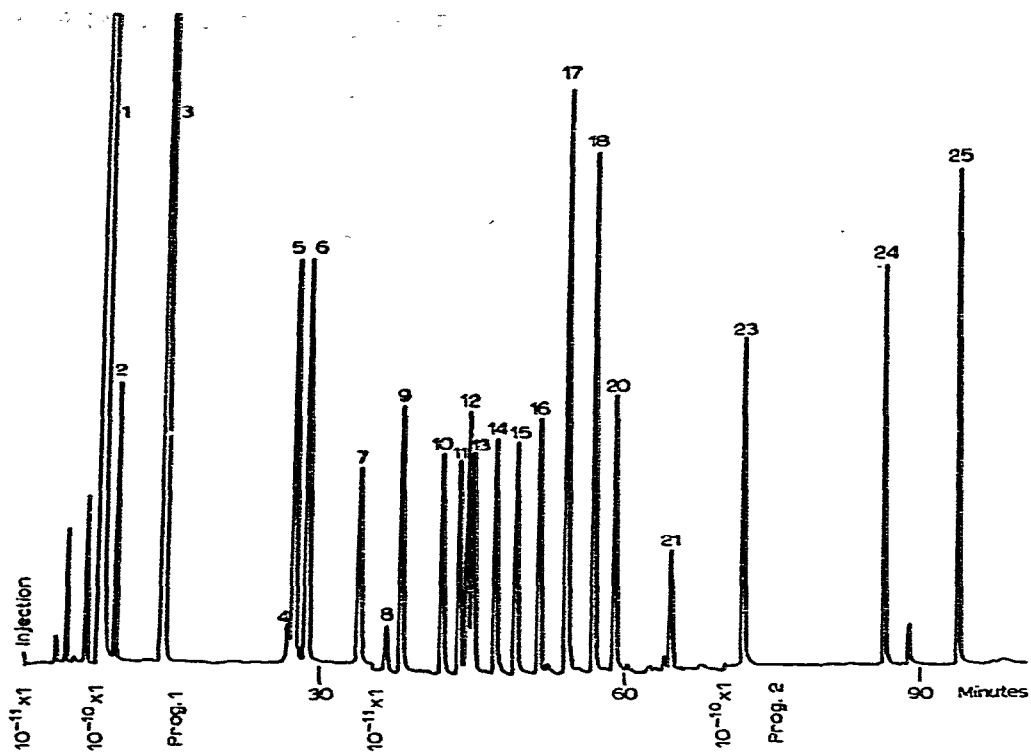


Fig. 3. Chromatogram of standard hydrocarbons (non-hydrogenated) using a capillary column.

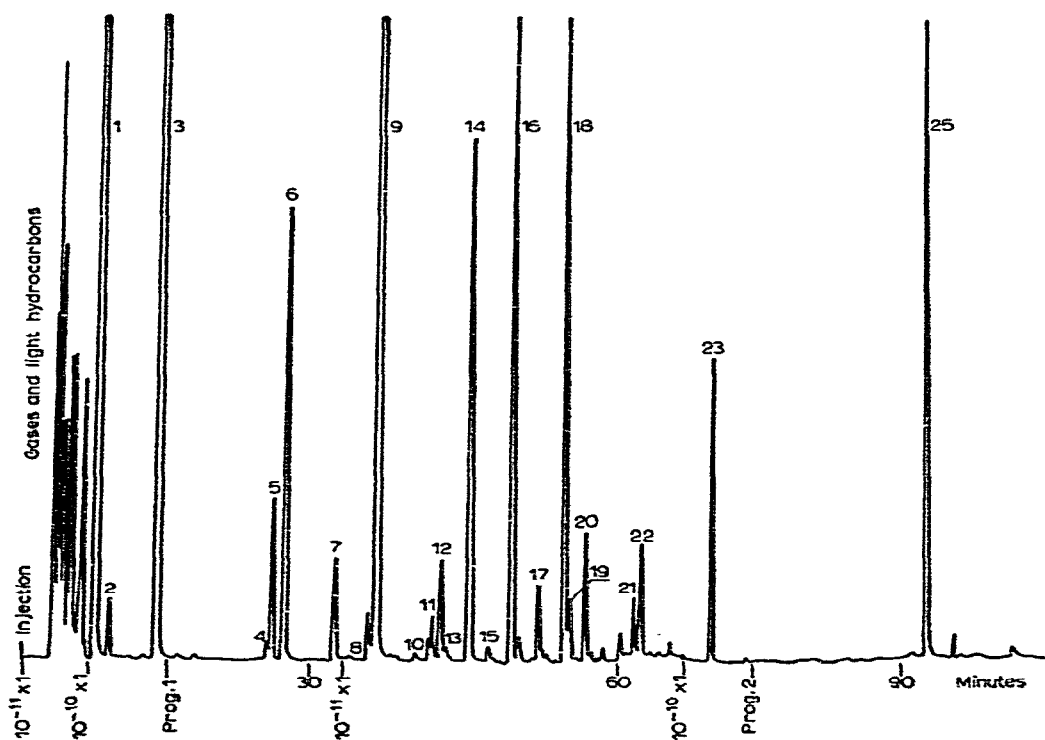


Fig. 4. Chromatogram of light oil (non-hydrogenated) using a capillary column.

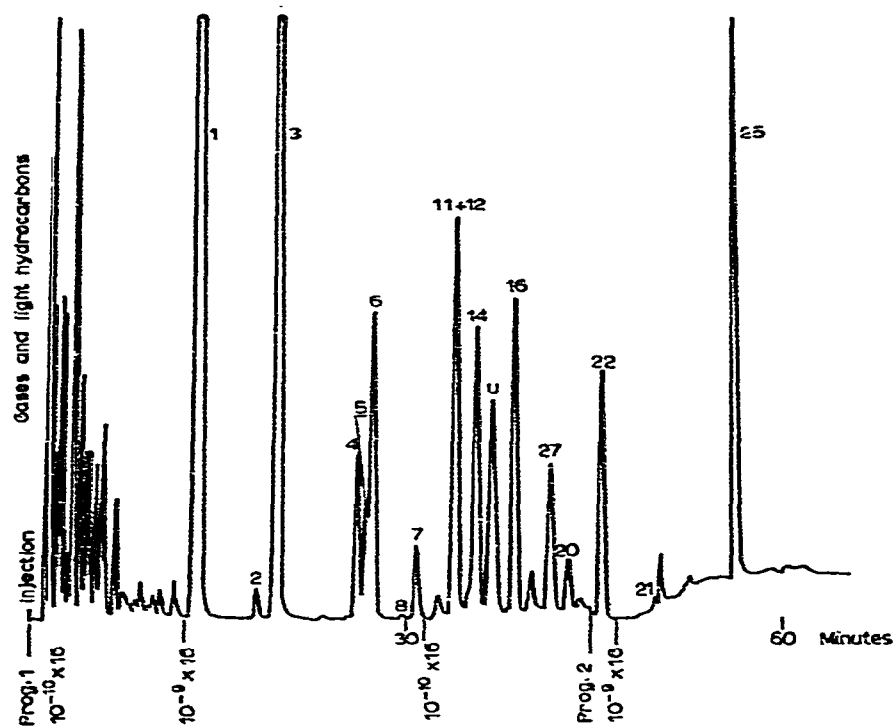


Fig. 5. Chromatogram of light oil using a copper catalyst for hydrogenation and an FFAP column.

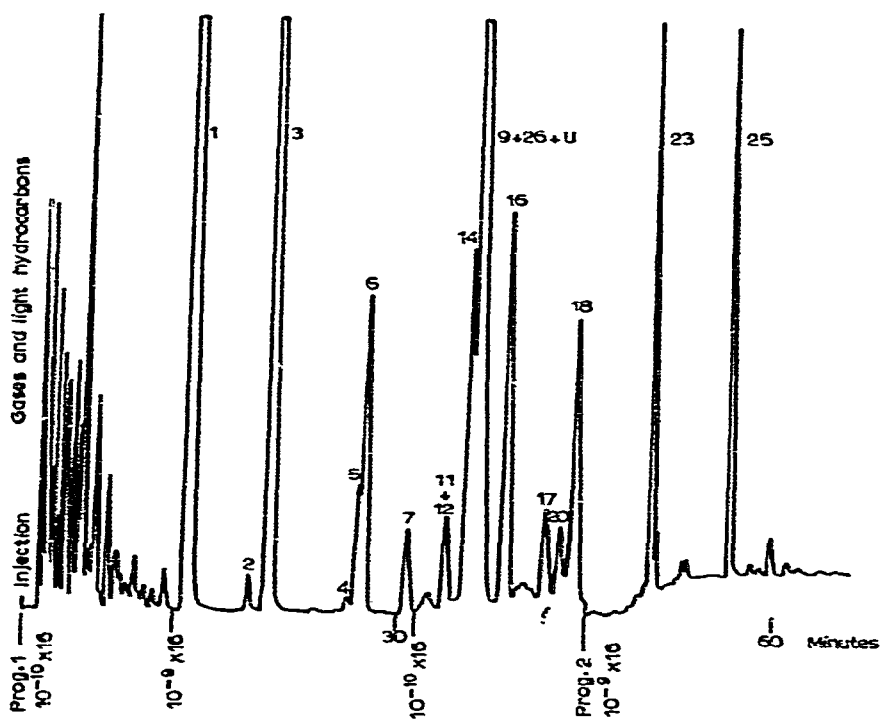


Fig. 6. Chromatogram of light oil (non-hydrogenated) using an FFAP column.

When using a capillary column there was no peak recorded due to dicyclopentadiene up to programme 2 (Figs. 3 and 4), but after hydrogenation dicyclopentadiene partially decomposed and the main peak (27) and two small peaks (D_1 and D_2) were observed (Figs. 1 and 2).

Finally, the following results were obtained from the peaks belonging to the compounds involved in the hydrogenation reaction.

(a) The shift of the peaks in the chromatograms due to hydrogenation was used to identify related compounds, for example, after hydrogenation α -methylstyrene in the light oil was identified by disappearance of peak (17) and an increase in the area of peak (8) (Figs. 1, 2 and 5).

(b) It was possible to calculate quantitatively even overlapping peaks by considering the differences between the areas under the peaks before and after hydrogenation.

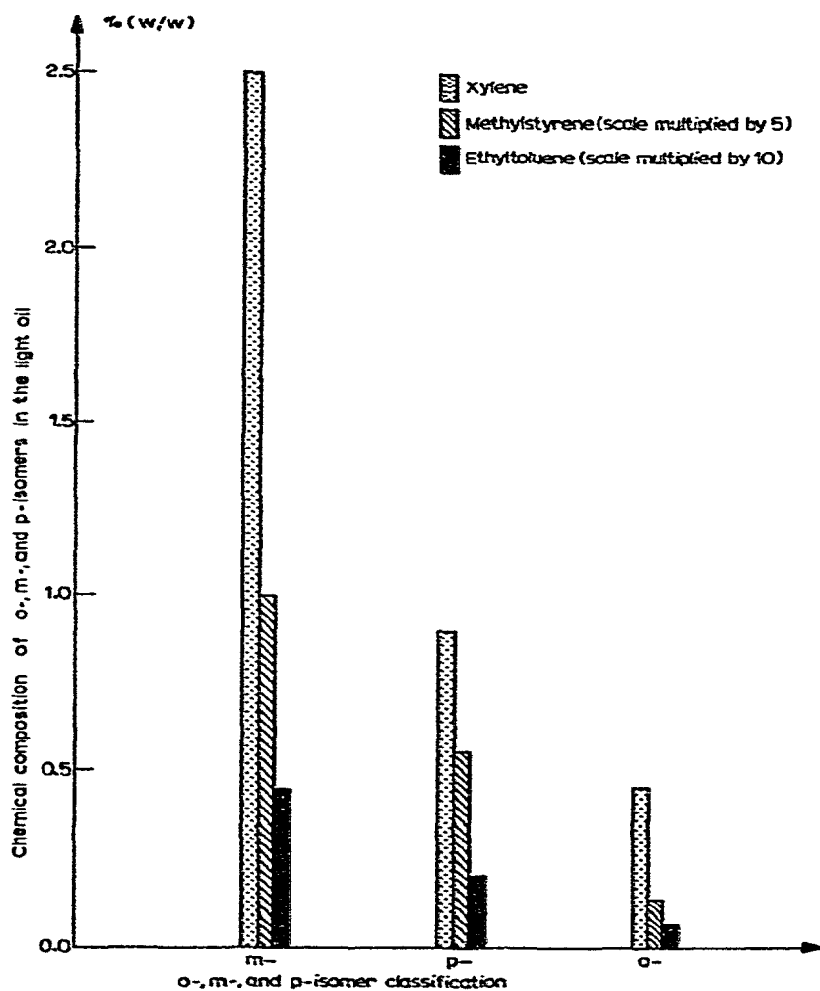


Fig. 7. Representative relationships of the composition of xylene, methylstyrene and ethyltoluene in terms of their *meta*-, *para*- and *ortho*-isomers in the light oil.

tion, e.g., the exact amount of styrene (9) was calculated from an increase in the peak area of ethylbenzene (4) or a reduction in the peak area of styrene (Figs. 5 and 6).

(c) Because certain peaks of the hydrogenatable and non-hydrogenatable compounds overlapped in the chromatograms, the catalytic hydrogenation process made it possible to eliminate the peaks belonging to the hydrogenatable compounds (e.g., indene, Figs. 5 and 6) and therefore to determine quantitatively the non-hydrogenatable compounds from the remaining peaks (e.g., coumarone, Figs. 5 and 6).

In addition to the identification and determination of styrene, indene, α -methylstyrene and *o*-methylstyrene, the actual amounts of *m*- and *p*-methylstyrenes (the unresolved peaks even with the capillary column, Fig. 4) were also obtained from the increased peak area of *m*- and *p*-ethyltoluene (Fig. 2). However, the increase in the peak area of *n*-propylbenzene is greater than expected from the hydrogenation of allylbenzene (Fig. 2) and is probably due to the presence of β -methylstyrene in the light oil, whose peak was not known and not well separated in the chromatograms. After hydrogenation the peaks of coumarone and thiophene remained unaffected owing to their heterogeneous rings.

The percentages of the isomers of methylstyrene, xylene and ethyltoluene in the light oil are shown in Fig. 7, and it is evident that the amounts of the isomers decrease in order *m*- > *p*- > *o*-.

The presence of thiophene or carbon disulphide destroys the catalytic effect of the metal walls of the injector and column when studying samples and standards in the non-hydrogenation process.

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