331. *The Production of Isoprene from Rubber.*

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For more than a century, researches have been carried out on the distillation of rubber, and the general nature of the products—isoprene, terpenes, and higher terpene compounds—has long been known, but comparatively little work has been done on the effect of variations in the conditions of distillation, and in particular, on the maximum possible yield of isoprene.

Williams (*Phil. Trans.*, 1860, **150**, 241), using an iron retort and distilling rubber at a relatively low temperature, obtained some 5% of crude isoprene, b. p. 37—44°. Fischer and Harries (*Ber.*, 1902, **35**, 2156) showed that when rubber is distilled at 0·25 mm., less than 1% of isoprene is obtained, and Staudinger and Fritschi (*Helv. Chim. Acta*, 1922, **5**, 785), working at 0·1—0·3 mm. and 275—320°, obtained 3·1%. These two results are not quite consistent, but they tend to show that a low pressure militates against a high yield of isoprene.

Staudinger and Geiger (*Helv. Chim. Acta*, 1926, **9**, 549) distilled rubber at ordinary pressure in an atmosphere of carbon dioxide and obtained 4·3% of crude isoprene. They also showed that rubber changes on heating, rapidly above 270°, to a " polycyclo-caoutchouc " which is more stable than ordinary rubber and does not yield isoprene on distillation. Midgley and Henne (*J. Amer. Chem. Soc.*, 1929, **51**, 1215) distilled large quantities of rubber (200 lb.) in 16-lb. batches by quickly raising the temperature of the retort to 700°. They thus obtained a 10% yield of isoprene, together with the three isomeric 2-methylbutenes resulting from its reduction, which occurred in the same fraction.

The very extensive work on the production of isoprene from terpenes has given rather contradictory results. By far the best yields claimed are those obtained by the method of Ostromisslenski (French Pat., 442980, 21/3/12) from dipentene, turpentine oil, etc. The method consists in boiling a mixture of the terpene and some low-boiling solvent, such as benzene, so that the vapour of the terpene is produced below its b. p. The mixed vapours are then passed over hot metallic wires and the products removed continuously. The vapours are produced at 95—115° and the yield is stated to be 80—90%.

In the present work an attempt was made to obtain the maximum yield of isoprene (1) from rubber directly, and (2) from the higher-boiling fractions obtained as by-products in (1). Various methods of distillation were tried, and the best results were obtained by dropping pieces of solid rubber on a hot surface and quickly removing and cooling the products. In this way a yield of 16·7% of pure isoprene was obtained. The higher-boiling fractions from this process were treated in various ways to obtain isoprene, and the best results came from a modification of Harries's "isoprene lamp." By combining the two processes, a total over-all yield of 23% was obtained.

We encountered much difficulty in estimating isoprene by the methods at present in use, none of which was entirely satisfactory. We now describe a new method, based on the Diels–Alder reaction with maleic anhydride, which gives accurate results when applied to mixtures not containing other butadienes. The presence of amylenes does not affect the results, which are definitely better than those obtained by the methods of Ostromisslenski (*J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1983) or Lebedev and Yakubchik (J., 1928, 823).

EXPERIMENTAL.

The rubber used was either smoked sheet or crêpe, of the following analysis (%):

	Moisture.	Ash.	Protein.	Resin.	Caoutchouc.
Smoked sheet......	0·52	0·34	2·18	2·93	94
Crêpe	0·79	0·14	2·04	2·02	95

All the final percentage yields are calculated on the wt. of raw rubber used. The type of retort employed is indicated under each expt. Condensation was effected by ice–salt, and frequently it was necessary to use two condensers in series. Temps. were ascertained by a thermocouple and were generally determined at the conclusion of an expt.

"*Standard Distillation.*"—For purposes of comparison, 250 g. of rubber were distilled from an Fe retort of 2 l. capacity during 4 hrs., the temp. being gradually raised to 580°. In this, and in all other distillations, the distillate was divided into four fractions: (1) up to 60°, containing isoprene; (2) 60—110°, containing C_6H_6, etc.; (3) 110—200°, containing dipentene and other terpenes; and (4) the remainder, containing polyterpenes, etc. The comparative amount of (2) indicated to some extent whether extreme pyrolysis with its consequent secondary changes had occurred, since when the distillate was produced at higher temps., this fraction increased.

Mean values for the "standard distillation" were: Total distillate, 94·5%. Fractions (1) 9·5%, (2) 5%, (3) 30%, (4) 50%. Fraction (1) contained 82·5% of isoprene.

Rapid Distillation.—The same procedure as before was followed, except that the temp. was raised as rapidly as possible to 650°. The whole operation occupied about 25 mins. The mean result was: Total distillate, 94·5%.

Fractions (1) 14·6% (83·6% of isoprene), (2) 3·1%, (3) 27·8%, (4) 49%. This result confirms the work of Midgley and Henne (*loc. cit.*).

Determination of the Point at which Isoprene is evolved.—The two expts. were repeated, but the distillate was collected in several cuts; with a slow distillation the whole of the isoprene came over in the first half of the time and the first 70% of the distillate. With a rapid distillation, however, isoprene occurred in all but the last of the cuts and in 90% of the total distillate.

Distillation of Rubber Solutions.—Solutions of rubber in fraction (3) were dropped slowly into a heated Cu retort. The best results were obtained from a 10% solution but only represented a 5·5% yield of fraction (1), the isoprene arising from the solvent being allowed for by means of a blank experiment.

Distillation of Molten Rubber.—Rubber was heated slowly till decomp. had proceeded far enough to permit of the residue being sufficiently fluid to flow at about 150°. Some distillate was collected during this heating and the fluid residue, maintained at about 150°, was dropped slowly into a heated Cu retort. The best results were obtained at about 600°, and under these conditions the total yield of fraction (1) was 11·6%. The process is slow and clearly has no advantage over a direct distillation.

Distillation of Solid Rubber.—For this distillation an apparatus was devised consisting of two pieces of Fe tube joined at right angles. The limbs were about 18″ long and the internal diameter 1″. Sheet-iron condensers were fitted on both limbs, and the apparatus was clamped so that one limb was horizontal and the other vertical. Fixed into the top of the vertical limb was a long glass tube (the inside tube of a condenser) closed at the upper end by a cork. The horizontal limb was connected to the condensing system.

To operate the retort, the joint between the two limbs, *i.e.*, the bottom of the vertical limb, was heated to the required temp., and small pieces of rubber were dropped down the glass tube by removing and quickly replacing the cork. By this means the solid rubber, without any preliminary heating, was brought practically instantaneously to the temp. of the retort. The volatile products were removed quickly, and any tendency for the vapours to escape through the glass tube prevented, by applying slight suction (about 3 mm. below atm. press.) to the end of the condensing system. The sheet-iron condenser on the horizontal limb of the retort cooled the vapours quickly below the temp., about 300°, at which isoprene polymerises to dipentene with any appreciable velocity.

In these expts., 100 g. of rubber (cut into 1 g. pieces) were used, and a distillation occupied about $1\frac{1}{2}$ hrs. Expts. were carried out over a wide range of temp. and the optimum temp. was found to be 590—600°, the yields falling off rapidly on both sides. Typical results were as follows :

	Total distillate, %.	Fractions, %.			
		(1).	(2).	(3).	(4).
540°	89	16·5	5·6	29·4	37·5
570	88·1	18·5	6·2	30·3	33·1
600	86·8	19·9	6·5	27·9	32·5
610	86·1	18·3	6·9	27·6	33·3
650	76·1	15·1	8·0	23·9	29·1

Fraction (1) contained an average of 84% of isoprene and this gives a max. yield of 16·7% of isoprene from the distillation of the rubber. The highest yield previously recorded was 10%, and as the isoprene was separated only by fractionation (Midgley and Henne, *loc. cit.*), it was probably not quite pure.

Cracking of Fractions (3) *and* (4).—Attempts were then made to obtain isoprene from fractions (3) and (4) by, in general, the methods usually employed in similar work on the terpenes. The figures recorded below refer in each case to the optimum temp.

(*a*) Fractions (3) and (4) separately dropped slowly into the Fe tube retort at 580—610° gave 7·2% and 4·4% respectively of fraction (1), which now contained only 72% of isoprene.

(*b*) An emulsion consisting of 100 g. of fraction (3) with 50 g. of H_2O, dropped slowly into a heated Cu retort, gave 6·8% of fraction (1) at 600—650°, and fraction (4) under similar conditions gave 3·6% of fraction (1) at 630—650°. It had been hoped that the steam produced would help to remove the vapours more quickly from the hot zone, but there was no advantage in the method.

(*c*) The vapour of fractions (3) and (4), passed separately through a heated SiO_2 tube, gave 7·5% and 4·4% respectively of fraction (1) at 580—610°.

(*d*) The vapour of fractions (3) and (4) was passed over a heated Pt wire in an apparatus similar to the " isoprene lamp " of Harries and Gottlob (*Annalen*, 1911, **383**, 228). A coil was made consisting of 1 m. of 0·01″ Pt wire wound on mica formers. This was suspended in a 1-l. Pyrex flask in such a position that the returning reflux liquid did not fall on the wire. The best results were obtained by using a current of 4·0—4·2 amps. at 200 volts, the distillate being taken from the top of an air-cooled reflux condenser. 100 G. of fraction (3) required 1 hr.'s treatment, and the yield was 17·4% of fraction (1), containing 78·2% of isoprene. The higher-boiling portions of the distillate were re-treated 3 or 4 times, giving decreasing yields each time, the total yield being 21·8% of fraction (1) and 17·2% of pure isoprene. Fraction (4) treated in the same way yielded very little isoprene. A very slight improvement in yield was obtained by diluting fraction (3) with C_6H_6 (cf. Ostromisslenski, *loc. cit.*).

Combining the yields from the above process with those from the distillation of solid rubber, a total yield of 23% of pure isoprene was obtained, calc. on the rubber used.

The Estimation of Isoprene.—Exhaustive expts. on the dichloro-compound method of Ostromisslenski and the sulphone method of Lebedev and Yakubchik showed that they give low results. By fractionation it is difficult to get strictly pure isoprene, and, moreover, during the process there is some loss by polymerisation. We therefore attempted to apply the Diels–Alder reaction for purpose of estimation. The procedure adopted is essentially that of Farmer and Warren (J., 1931, 3221). A weighed quantity of the mixture to be estimated was distilled from Na to remove traces of H_2O. About 10 g. of pure C_6H_6 were weighed into a tared, well-stoppered bottle, about 2 g. of the mixture added, the whole weighed, and immediately placed in ice–salt. Just over 4 g. of commercial maleic anhydride (m. p. 54°) (rather more than twice the expected wt. of isoprene in the mixture) were weighed into a beaker and warmed with about 10 g. of pure benzene until dissolved. The solution was cooled and poured into the tared bottle, which was immediately stoppered and returned to the ice-chest for 12 hrs. The exact wt. of maleic anhydride added was found by evaporating the few drops of C_6H_6 left in the beaker, weighing the residue, and subtracting this from the original wt. taken. The contents of the bottle were next transferred to a Carius tube, and the sealed tube heated at 100° for 2 hrs. After cooling, the contents of the tube, together with the C_6H_6 washings, were evaporated at room temp. and reduced press. On adding pure dry Et_2O to the residue and again evaporating in the same way, dry white crystals were obtained and weighed. The gain in wt. of the maleic anhydride represented the wt. of isoprene present in the original mixture.

The method was tested by preparing strictly pure isoprene from the sulphone and then estimating its purity. Duplicate expts. in each case gave a result of exactly 100%. Further, mixtures were made of this pure isoprene with amylenes, and the results confirmed the accuracy of the method. Details of one determination are given :

$$\text{Mixture}\begin{cases}\text{Amylenes, } 1{\cdot}5120 \text{ g.}\\ \text{Isoprene, } 1{\cdot}7925 \text{ g.}\end{cases}$$

Maleic anhydride, 4·2613 g.
Compound recovered, 6·0534 g.
Isoprene found, 1·7921 g.

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