

THERMAL DIMERIZATION OF CYCLOPENTADIENE AND ITS REACTION WITH ISOPRENE

By

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Properties and utilization of cyclopentadiene

Cyclopentadiene (CPD) is a colourless compound with a characteristic smell, with the following main physicochemical characteristics: [1-3]:

Molecular weight	66.1
Boiling point	41 °C
Melting point	-85 °C
Density d_4^{20}	0.8021 g/cm ³
Density d_4^{25}	0.7966 g/cm ³
Refractive index n_D^{20}	1.4462
Refractive index n_D^{25}	1.4404
Heat of combustion	10,600 cal/g
Chemical constitution	-----



A characteristic feature of CPD is to react with another CPD molecule conforming to the mechanism of diene synthesis. This reaction takes place already at ambient temperature at an appreciable rate. In the course of 24 hours, about 50% of pure CPD are converted into dicyclopentadiene (DCPD) [4, 5]:

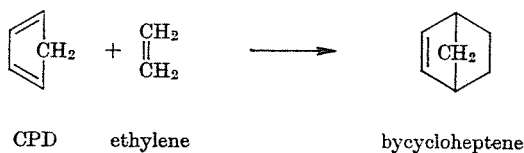


Two structures of DCPD exist: in endo-cis-DCPD the two five-membered interconnected rings are so positioned that one is below the other, while in exo-cis-DCPD the rings are beside each other. Endo-cis-DCPD is formed at dimerization temperatures below 150 °C, while at higher temperatures exo-cis-DCPD is formed [5]. Endo-cis-DCPD decomposes at its boiling point (170 °C) to yield CPD.

Owing to its double bonds and to the active methylene group enclosed between the double bonds, CPD is highly reactive. Accordingly, its main reactions can be divided into two groups: those of the double bonds and those of the methylene group.

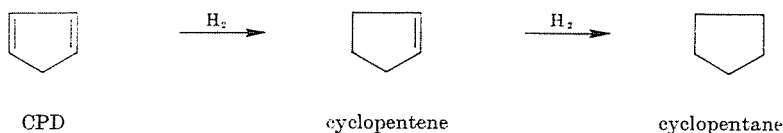
Important reactions of the double bonds [6, 7]

(i) Diels–Alder reaction (diene synthesis). In this reaction the conjugated diene (CPD) is added onto a double bond, e. g. the reaction of CPD and ethylene:

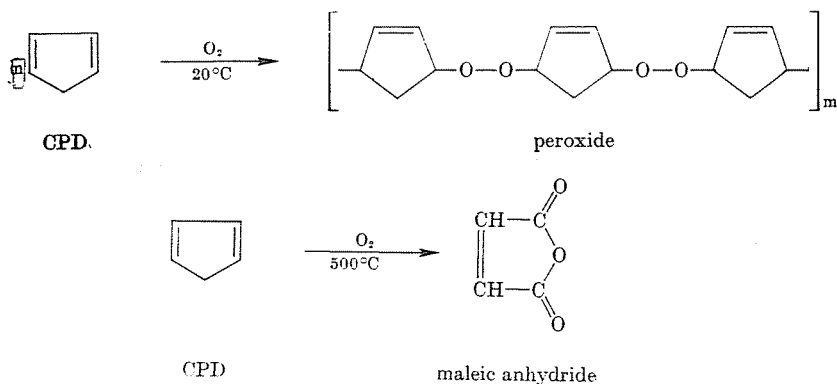


Numerous Diels–Alder reactions of CPD are known [7].

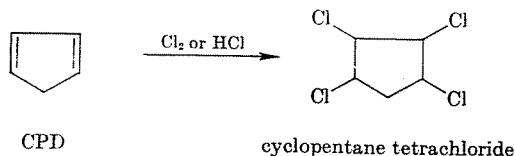
(ii) Hydrogenation of CPD yields cyclopentene and cyclopentane:



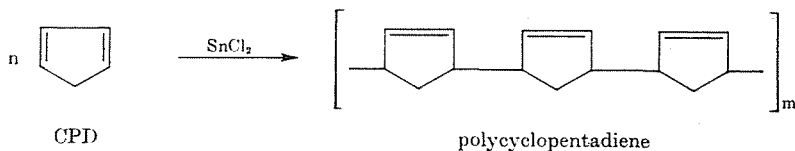
(iii) Oxidation at low temperatures yields an explosive peroxide. At higher temperatures, in the vapour phase, maleic anhydride is obtained:



(iv) With molecular chlorine or hydrochloric acid, chlorinated derivatives with different chlorine contents up to cyclopentane tetrachloride are obtained:

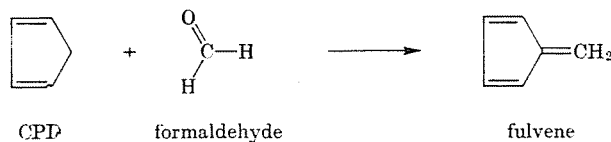


(v) Polymerization in the presence of tin chloride catalyst, under exclusion of air, yields polycyclopentadiene:

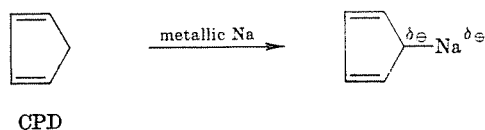


Important reactions of the methylene group [6, 8, 9]

(i) The most characteristic reaction of the methylene group in CPD is fulvene formation. This takes place in alkaline solution with carbonyl compounds such as formaldehyde, acetone, benzaldehyde etc.:



(ii) Only small energy is required to split off a proton from the CH_2 group, and hence the compound tends to carbanion formation. While open-chain 1,3-dienes, e.g. butadiene, yield a polymerizable adduct under the effect of metallic sodium, CPD forms a relatively stable compound, sodium cyclopentadienate, which is incapable of polymerization:



The compound is similar to a salt, it decomposes before melting and is insoluble in most hydrocarbons. The stability of the cyclopentadienate anion is due to the aromatic sextet established from the π electrons of the double bonds and the free electron pair of the anionoid carbon atom. Numerous metal compounds of CPD have been synthesized, among which the best known is ferrocene (iron(II)dicyclopentadienyl).

Utilization of CPD and DCPD [10–13]

Both CPD and DCPD have found multiple fields of utilization. Major uses involve the Diels–Alder reaction products and their derivatives. Manifold application is ensured by the active double bond of the bicycloheptene structure formed in these reactions, since it allows the modification of the molecule with various functional groups. The derivatives obtained in this manner are successfully used in the paint industry, in the dye industry and in the manufacture of pesticides. Other known applications are additives to lubricants, plasticizers, antioxidants, thermal stabilizers.

Among CPD derivatives obtained from other than Diels–Alder reactions, polycyclopentadiene is utilized in the paint industry, and cyclopentene manufactured by selective catalytic hydrogenation of CPD is the monomer of the elastomer *trans*-1,5-poly-pentamer.

Occurrence and manufacture of CPD

Formerly CPD was recovered from the forerun of benzene in coking plants where it is present in amounts of 3 to 5 per cent by weight. More recently, the availability of CPD has been substantially enlarged by utilizing the C_5 fraction obtained in the pyrolysis of petroleum products. The composition of the C_5 fraction and its CPD content varies in wide limits depending on the feed and on pyrolysis parameters. In Table 1, the composition of the C_5 fraction of naphtha pyrolysis under medium and sharp conditions is listed.

According to the statements of Soviet researchers [14], for the case of commercial-scale light naphtha pyrolysis, maximum CPD yield is obtained at 750 °C. It amounts to about 0.8 per cent by weight of the feed, that is, 8500 to 10,000 tons per year of CPD in a 250,000 ton p.a. ethylene plant, thereby increasing the economics of pyrolysis and supplying valuable starting material for producing many chemicals.

There are two groups of technologies for the recovery of CPD, namely the thermal methods and the extractive distillation methods, eventually combined with thermal operations.

The *thermal method* [15, 16] is based on the reversible dimerization of CPD. It consists essentially in the single-stage conversion of the CPD content in the C_5 fraction (or in the benzene distillation forerun) into DCPD by thermal dimerization. The boiling point of DCPD being 170 °C, it is readily separated by distillation from the other, lower-boiling components of the C_5 fraction.

The thermal treatment is carried out at 80 to 120 °C for 2 to 7 hours at a slightly increased pressure (at the vapour pressure of the hydrocarbons for the given temperature). The DCPD obtained has a purity of 90 to 93%, its impurities consisting of co-dimers formed with other dienes of the C_5

Table 1
Typical composition of C₅ fraction

Hydrocarbon	Medium depth pyrolysis %	Sharp pyrolysis %	Boiling point °C
<i>C₄ hydrocarbons</i> (without acetylenes)	3.3	1.1	
<i>C₅ saturated hydrocarbons</i>			
i-pentane	8.3	8.1	27.8
n-pentane	10.3	10.5	36.1
cyclopentane	1.6	1.0	49.3
<i>C₅ olefinic hydrocarbons</i>			
3-methyl-1-butene	1.0	0.2	20.1
1-pentene	4.1	2.5	30.0
2-methyl-1-butene	5.6	3.0	31.2
trans-2-pentene	2.5	2.2	36.4
cis-2-pentene	1.9	0.8	36.9
2-methyl-2-butene	3.6	3.9	38.6
cyclopentene	5.6	3.6	44.2
<i>C₅ dienes</i>			
1,4-pentadiene	1.5	1.0	26.0
isoprene	18.6	19.6	43.1
3-methyl-1,2-butadiene	200 p.p.m.	300 p.p.m.	40.7
cyclopentadiene	15.2	27.6	40.8
trans-1,3-pentadiene	9.6	8.5	42.0
cis-1,3-pentadiene	6.2	5.1	44.1
1,2-pentadiene		—	44.9
2,3-pentadiene	0.4	—	48.3
<i>C₄ and C₅ acetylene derivatives</i>			
2-butine	0.4	1.0	27.0
isopropylacetylene	150 p.p.m.	500 p.p.m.	29.3
isopropenylacetylene	500 p.p.m.	0.2	32.5
1-pentine	200 p.p.m.	200 p.p.m.	39.7
2-pentine	200 p.p.m.	—	56.0
<i>C₆+ derivatives</i>	0.3	0.1	..

fraction. CPD is recovered from DCPD by liquid-phase or vapour-phase depolymerization. The flow chart of the process is shown in Fig. 1.

Purity of DCPD and hence of CPD can be improved up to 95 to 96% by repeated dimerization, subsequent rectification and depolymerization [17].

The *extractive distillation method* [18–20] has primarily been developed with the aim of isoprene recovery. Polymerization grade isoprene must not contain more than 1 p.p.m. CPD. This requirement, as well as the good market potential for CPD largely contributed to the realization of CPD recovery. A simplified general schematic diagram of the process is shown in Fig. 2.

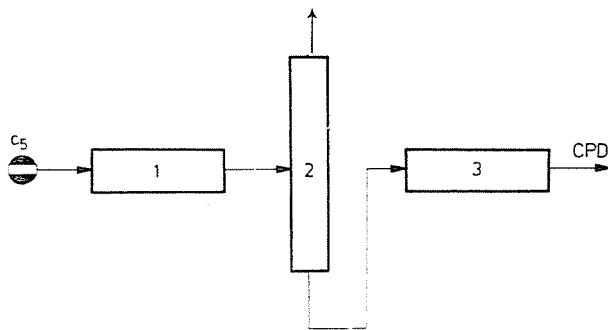


Fig. 1. Flow chart of the thermal process; 1 — dimerization, 2 — rectification, 3 — monomerization

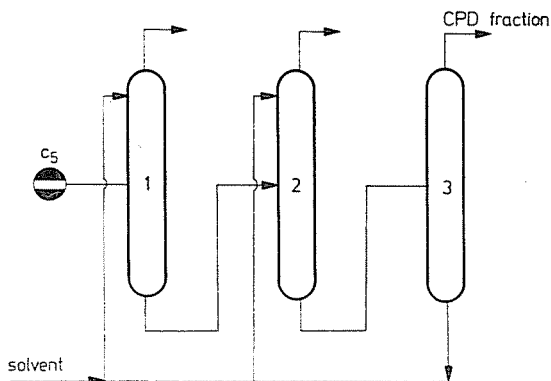


Fig. 2. Flow chart of the extractive distillation process; 1 — extractive distillation, 2 — extractive distillation, 3 — solvent removal

The C_5 fraction which has previously been separated from C_4 and C_6 components by two-stage distillation is introduced into the middle section of the extractive distillation column 1, while solvent is fed to the top of the column. The overhead product is a raffinate rich in paraffins and olefins. The bottom product containing the dienes is led into the second extractive distillation column 2, where further separation takes place. The overhead product is the CPD fraction. This is separated from the solvent in the column 3. Acetone acetonitrile dimethylformamide N-formylmorpholine, N-methyl-

pyrrolidone are used as solvents. CPD is eventually recovered from the CPD fraction by means of the above-described thermal method.

Besides these commercial methods for CPD recovery we wish to mention that CPD can also be separated from aliphatic hydrocarbons by selective precipitation with nickel tetra(8-picoline)-dithiocyanate. This method is based on the tendency of CPD to complex formation [21],

Experimental

The recovery of CPD by thermal methods requires the fundamental knowledge of the chemical reactions taking place in course of the process. As a first step, we studied the kinetics of CPD dimerization.

Studies of CPD dimerization

We used model mixtures composed of a hydrocarbon fraction with an end point of 50 °C (boiling point of the C₅ fraction) and freshly distilled CPD. The hydrocarbon fraction used as solvent does not affect the dimerization of CPD. The CPD content of the model mixture was set to 10–15 per cent by weight. The reaction was observed at 60, 80, 100 and 120 °C, resp.

Steel pressure vessels with capacities of 12 cm³ have been prepared for the experiments. Identical amounts (8 cm³) of the initial mixture were introduced into the vessels. Carefully sealed they were placed all at the same time into a thermostat. After 0.5, 1, 2, 3, and 4 hours, the pressure vessels were transferred into a salted ice bath to chill the reaction. After cooling, the reaction mixture underwent rapid gas chromatographic analysis. The concentrations measured will be termed *C* in the followings. Simultaneously with placing the pressure vessels into the thermostat, the initial mixture was also analyzed (*C*₀).

Gas chromatography conditions were as follows:

Type	CHROM-3
Length of column	2600 mm
Packing	PEGA
Thermostat temperature	50 °C
Evaporizer temperature	100 °C
Carrier gas	nitrogen
Pressure of carrier gas	0.5 bar gauge pressure
Detector	flame ionization
Sensitivity	1/500
Amount of sample	0.08 μl
Speed of paper	10 mm/min

The experimental results are summarized in Table 2.

By plotting $\left(\frac{1}{C} - \frac{1}{C_0}\right)$ values against reaction time τ straight lines were obtained for each studied temperature. This indicates that dimerization of CPD within the studied temperature range is a second-order reaction. From the slope of the straight lines, the following rate constants were found:

At 60 °C	$k = 0.065 \text{ dm}^3 \cdot \text{mol}^{-1} \text{h}^{-1}$
At 80 °C	$k = 0.267 \text{ dm}^3 \cdot \text{mol}^{-1} \text{h}^{-1}$
At 100 °C	$k = 0.960 \text{ dm}^3 \cdot \text{mol}^{-1} \text{h}^{-1}$
At 120 °C	$k = 3.000 \text{ dm}^3 \cdot \text{mol}^{-1} \text{h}^{-1}$

By plotting the rate constants determined at different temperatures against the reciprocal temperature to log scale a straight line was obtained, that is, the rate constant of the reaction is related to temperature according to the Arrhenius equation

$$k = A \cdot e^{-\frac{E}{RT}}$$

From the slope of the straight line the activation energy was found to be $E = 16400 \text{ cal} \cdot \text{mol}^{-1}$, and from the intercept with the ordinate axis the pre-exponential factor was $A = 7.1 \cdot 10^9 \text{ dm}^3 \cdot \text{mol}^{-1} \text{h}^{-1} = 1.94 \cdot 10^6 \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}$.

Accordingly, our experiments demonstrated the dimerization of CPD in light naphta solvent to be a second-order reaction, and the value of the rate constant:

$$k = 1.94 \cdot 10^6 e^{-\frac{16400}{RT}} \text{ dm}^3 \text{mol}^{-1} \text{s}^{-1}.$$

This result is in good agreement with data from the literature [4].

Table 2
Dimerization of cyclopentadiene

Reaction time, hours,	CPD content, mol · dm ⁻³			
	60 °C	80 °C	100 °C	120 °C
0	1.242	1.128	0.934	0.891
0.5	1.235	...	0.739	0.438
1	...	1.002	0.578	0.267
1.5	1.136	0.831	...	0.205
2	...	0.814	0.354	0.142
2.5	1.060	0.121
3	...	0.690	0.278	...
4	...	0.556	0.210	...

According to our control-measurements no monomerization of the DCPD occurs in the studied temperature range.

Study of CPD dimerization in the presence of isoprene

Among the dienes present in the C₅ fraction besides cyclopentadiene, mainly its reaction with isoprene must be taken into consideration. We therefore carried out laboratory experiments to study thermal dimerization of cyclopentadiene in the presence of isoprene. Rather than to use the C₅ fraction supplied by the ethylene plant, model mixtures were prepared from characteristic hydrocarbons, in order to eliminate the interference from other reactions of minor importance as well as difficulties in analysis.

The model mixtures consisted of CPD, isoprene and of two solvents, namely benzene and n-hexane, which both are inert with respect to the reaction in question. Both CPD and isoprene (IPN) were distilled before use. The composition of the model mixtures varied between the following limits:

CPD	6 to 17% by weight
IPN	16 to 24% by weight
Benzene	22 to 24% by weight
n-Hexane	44 to 48% by weight

The isoprene to cyclopentadiene ratio in the various model mixtures was about 4 : 1, 2 : 1 and 1 : 1. In the C₅ fraction from the ethylene plant this ratio was about 1 : 1. However, in order to achieve deeper knowledge on the reaction, we also utilized higher isoprene proportions.

The experiments were carried out in 12 cm³-volume steel pressure vessels. 8 cm³ of the model mixtures were introduced into each vessel and these were then placed into an ultrathermostat. Dimerization was performed at 80, 100, 120 and 150 °C. After the required periods of time the pressure vessels were cooled in salted ice and the composition of both the initial model mixtures and the product was determined using the following gas chromatography conditions:

Type of gas chromatograph	CHROM-3
Length of column	1200 mm
Packing	AP-L (Apiezon)
Temperature of thermostat	60 °C + 15 °C/min up to 140 °C
Temperature of evaporizer	120 °C
Carrier gas	nitrogen
Pressure of carrier gas	0.5 bar gauge pressure
Detector	flame ionization
Sensitivity	1/1000 to 1/100
Amount of sample	0.02 · 10 ⁻⁶ dm ³
Speed of paper	5 to 10 mm/min

A typical chromatogram of the reaction product is presented in Fig. 3. The peak preceding the DCPD peak represents the co-dimer (CDM) formed by addition of isoprene and cyclopentadiene. Increasing the sensitivity some additional peaks could be detected, their total amount being below 1%.

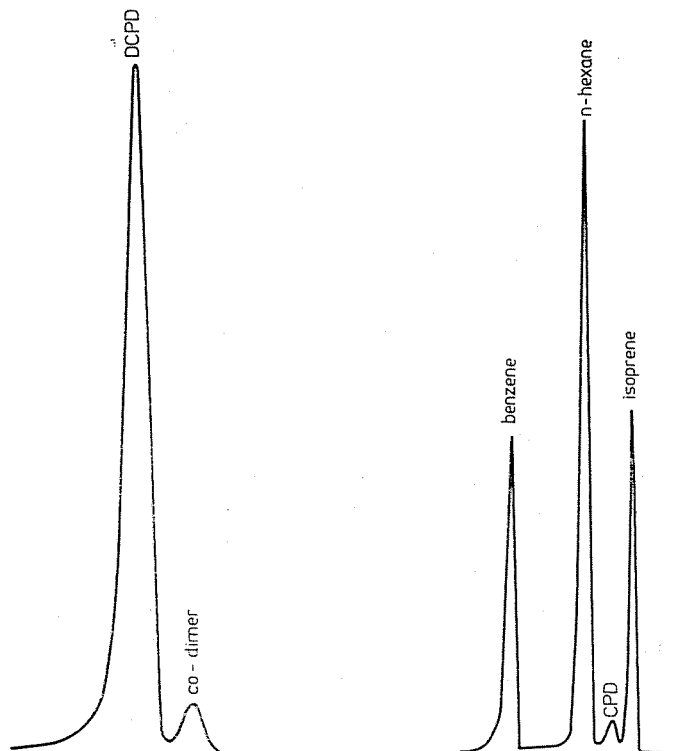


Fig. 3. A typical chromatogram of the reaction product

The structure of the co-dimer was established indirectly. The solvent and the unreacted compounds were stripped off. The residue consisted of DCPD and CDM and was subsequently subjected to thermal depolymerization. The chromatogram of the product demonstrated the presence of IPN in addition to CPD, confirming that the co-dimer contained isoprene. The chromatogram of the product obtained with pure isoprene exhibited the presence of neither DCPD nor CDM.

From among the results of experiments carried out with various IPN : CPD ratios, data obtained with 1 : 1 ratio model mixtures are listed in Table 3. Concentration of the reaction products at 100 °C *versus* reaction time are presented in Fig. 4.

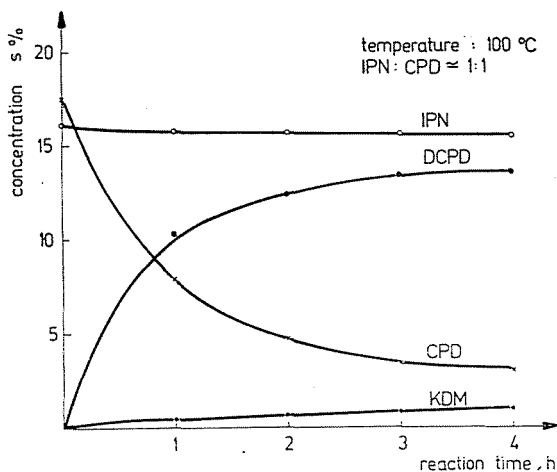


Fig. 4. Concentration of the reaction product vs. reaction time

Table 3

Dimerization of cyclopentadiene in the presence of isoprene

Temperature °C	Reaction time, h	Cyclopentadiene, % by wt	Isoprene % by wt	Dicyclopentadiene, % by wt	Co-dimer % by wt
80	0	9.2	12.9	—	—
	1	7.5	12.9	2.1	—
	2	5.4	12.9	3.7	—
	3	4.7	12.8	3.3	0.2
	4	4.3	12.8	4.8	0.3
100	0	17.5	16.0	—	—
	1	7.9	16.0	10.1	0.5
	2	4.8	15.9	12.4	0.6
	3	3.5	15.7	13.4	1.0
	4	3.3	15.7	13.7	1.0
120	0	18.0	15.8	—	—
	1	4.4	15.3	13.0	0.9
	2	2.9	15.1	14.4	1.3
	3	2.0	15.0	15.1	1.6
	4	1.8	14.9	15.3	1.6
150	0	18.1	14.5	—	—
	1	2.4	13.3	14.5	2.4
	2	1.9	13.0	14.7	2.9
	3	1.9	12.9	14.2	3.3
	4	1.8	12.9	14.7	3.0

The data allow to conclude that the reactions of DCPD and CDM formation proceed simultaneously. Both CPD and isoprene conversion increase with increasing temperature and reaction time, and correspondingly the amounts of DCPD and CDM also increase.

Furthermore we found that of the simultaneous reactions, the formation of DCPD is substantially faster. The rate of this reaction increases to a greater extent with temperature than that of co-dimer formation.

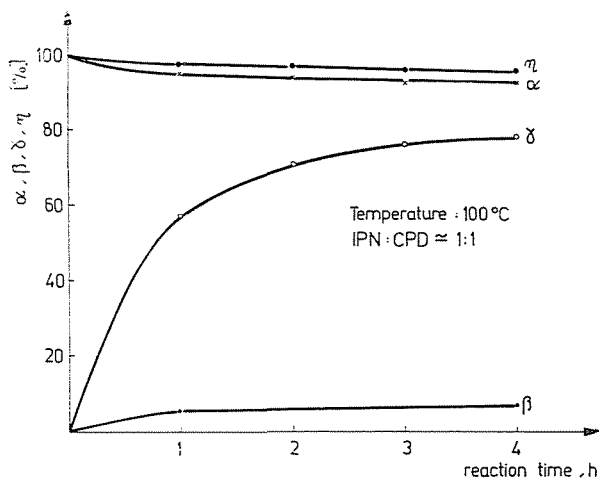


Fig. 5. Characteristics of the dimerization reaction *vs.* reaction time

Technological parameters of the thermal recovery of CPD are of decisive importance to the purity and yield of the product. We utilized our experimental data to study these questions, and calculated the following characteristics for this purpose:

$$\eta, \% = \frac{\text{DCPD}}{\text{reacted CPD}} \cdot 100 \quad \text{characterizing the efficiency of the reaction}$$

$$\alpha, \% = \frac{\text{DCPD}}{\text{total dimer formed}} \cdot 100 \quad \text{characterizing the purity of DCPD}$$

$$\beta, \% = \frac{\text{CDM}}{\text{total dimer formed}} \cdot 100 \quad \text{characterizing the amount of co-dimer in the product}$$

$$\gamma, \% = \frac{\text{DCPD}}{\text{initial CPD}} \cdot 100 \quad \text{i.e. DCPD yield}$$

The change of these characteristic values with reaction time at 100 °C is presented in Fig. 5, demonstrating DCPD yield to increase with time, whereas the efficiency of the reaction and the purity of the DCPD decreases. We wish to note that efficiency and purity values were worse with model

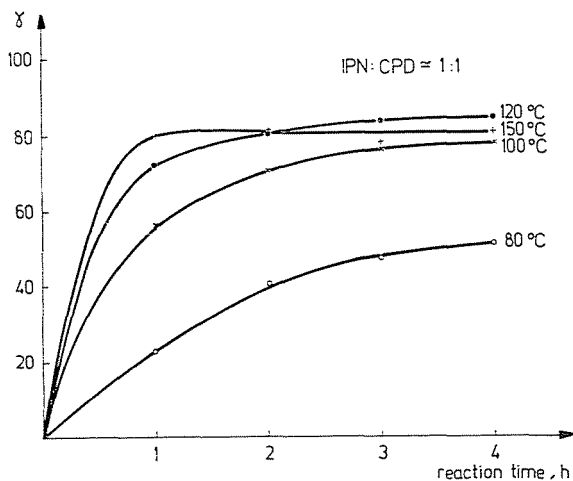


Fig. 6. DCPD yield vs. reaction time

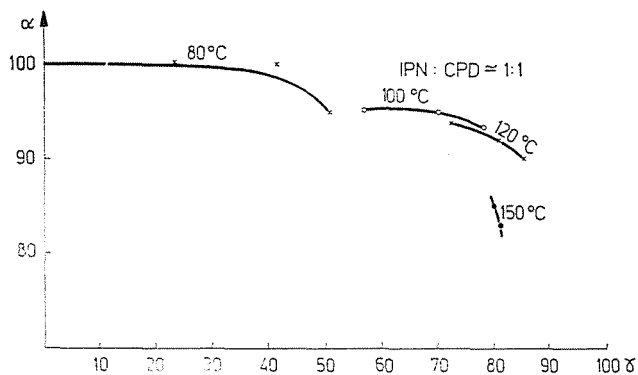


Fig. 7. Purity of DCPD product vs. yield at different temperatures

mixtures containing higher amounts of isoprene (IPN : CPD = 4 : 1 and 2 : 1). In the end product of the experiments carried out at 150 °C other impurities were also present.

DCPD yields vs. reaction time at different temperatures are shown in Fig. 6. It may be observed that at 120 °C, 80% of CPD is converted into DCPD, and this value increases only slightly with increasing reaction time. At 100 °C, substantially longer reaction time is required to achieve a yield of 80%.

Besides yield, purity of the formed DCPD is of major importance. Information on this question is obtained from Fig. 7, presenting DCPD/total product as a function of yield. No great difference can be observed between the isotherms at 100 and at 120 °C. However, reaction times are more favourable in the case of the higher temperature.

Summing up, it can be concluded that cyclopentadiene can be recovered by thermal dimerization from a mixture of cyclopentadiene and isoprene, since the side reactions proceed at a lower rate. Experimental data demonstrate DCPD yield to be around 80%, this can be increased by not more than a few per cent. Optimum parameters appear to be 120 °C and 2 hours reaction time, where the purity of DCPD is 95%.

Summary

A short survey of the major physical and chemical properties of cyclopentadiene is given, and methods for the recovery of cyclopentadiene from the C₅ fraction of naphtha pyrolysis are described. Dimerization, the basic reaction of thermal recovery was experimentally investigated. Dimerization was carried out in the presence of isoprene at different temperatures between 80 and 150 °C. It was found that in addition to dicyclopentadiene, a co-dimer of isoprene and cyclopentadiene also formed. The diagrams demonstrate the effect of technological parameters on the yield and purity of dicyclopentadiene.

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