

## AROMATISATION OF 1,3-BUTADIENE UNDER PRESSURE

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(Received 13 July 1990)

### ABSTRACT

The aromatisation of 1,3-butadiene has been performed under pressure in inert and reactive atmospheres. The influence of industrial catalysts has also been studied. The results, as expected, show that pressure plays an important role in the Diels–Alder reaction of the dimerisation of 1,3-butadiene to 4-vinylcyclohexene.

The catalysts used are not efficient in view of the high yield of light aromatic hydrocarbons.

A three-step procedure is proposed to optimise the aromatisation of short chain olefins.

### INTRODUCTION

Benzene, toluene and xylene (BTX fraction) are important feedstocks for the chemical industry. The price of these chemicals underlines the importance of being able to use coal, or particular fractions derived therefrom, to produce light aromatic hydrocarbons.

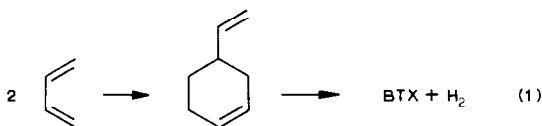
The literature on paraffinic hydrocarbon cracking is abundant, mainly because of its impact on petrochemistry. The aliphatic hydrocarbon content in coal and primary tars has also been extensively studied. In recent years, it has once again been studied by numerous researchers, amongst them Calkins et al. [1,2] and Snape et al. [3].

In our laboratory, much work has been done on the thermal cracking at atmospheric pressure of *n*-decane, chosen as a model compound for the long-chain hydrocarbons [4,5] present in primary tars, and on the thermal cracking of butane, isobutene [6], and 1,3-butadiene [7] as models for the short-chain hydrocarbons, with respect to the formation of light aromatic hydrocarbons. It was shown that the latter are formed by Diels–Alder reactions between the short-chain olefins produced by successive cracking of the paraffins. In this mechanism, 1,3-butadiene plays an important role as

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previously shown by various authors [7–10]. Dimerisation of 1,3-butadiene leads to 4-vinylcyclohexene and this dehydrogenates to produce light aromatics



The first step should be thermodynamically favoured by the pressure. A few authors [11,12] have investigated the influence of the pressure on the dimerisation of butadiene or butadiene derivatives but at low temperature ( $-120$ – $60^\circ\text{C}$ ) and high pressure (15–50 kbar). The purpose of this work is to study the influence of pressure (between 0.1 and 5 MPa) on the aromatisation of 1,3-butadiene. Some experiments have been performed in the presence of industrial catalysts.

## EXPERIMENTAL

The schematic diagram of the installation is given in Fig. 1. The stainless steel reactor is able to support a pressure of 6 MPa at  $900^\circ\text{C}$ . Figure 2 shows a detail of the reactor.

Analyses of the gases and liquids were performed using gas chromatography. Liquids were analysed on an SP 2100 capillary column (60 m long, 0.25 mm i.d.) maintained at  $40^\circ\text{C}$  for 25 min and then heated at  $2^\circ\text{C min}^{-1}$  up to  $250^\circ\text{C}$ , with a nitrogen flow rate of  $0.5 \text{ ml min}^{-1}$ . Quantitative analysis

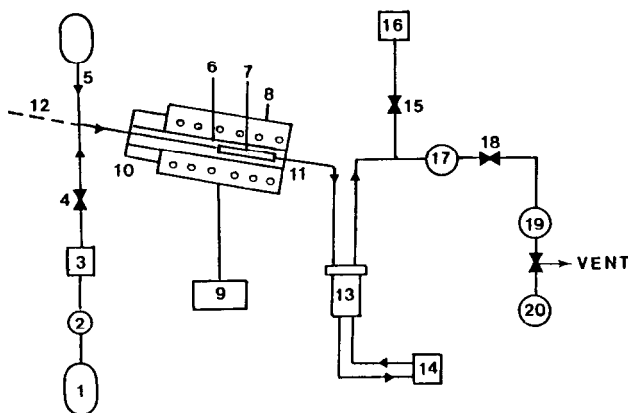


Fig. 1. Schematic diagram of the installation: (1) 1,3-butadiene cylinder; (2) flowmeter; (3) HPLC pump; (4) flow regulator valve; (5)  $\text{N}_2$  or  $\text{H}_2$  entrance; (6) stainless steel tube; (7) reactor; (8) electric furnace; (9) temperature regulator; (10, 11) pre- and post-heaters; (12) thermocouple; (13) trap; (14) cryostat; (15) atmospheric pressure reducing valve; (16) vacuum pump; (17) pressure gauge; (18) output metering valve; (19) gas meter; (20) gas collector.

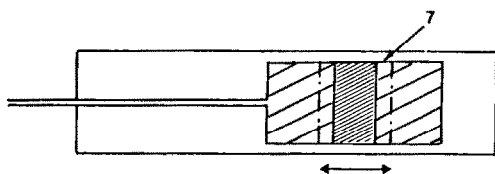


Fig. 2. Detail of the reactor: 7, reactor;  $\longleftrightarrow$ , isothermal zone (4.8 cm);  $\square\square\square$ , quartz wool;  $\text{▨}$ , catalyst or inert.

was by the internal standard (tetralin) method.  $\text{H}_2$ ,  $\text{CH}_4$  and  $\text{C}_2\text{H}_6$  were analysed on a 4 m long active carbon column maintained at  $180^\circ\text{C}$  with a nitrogen flow rate of  $60\text{ ml min}^{-1}$ , using a catharometer detector.  $\text{C}_3\text{--C}_5$  hydrocarbons were separated on a 2 m long Carbopack column with a helium flow rate of  $50\text{ ml min}^{-1}$ . The temperature was maintained at  $40^\circ\text{C}$  for 3 min and then heated at  $4^\circ\text{C min}^{-1}$  up to  $98^\circ\text{C}$ . An FID detector was used.

Three industrial catalysts were also investigated. Catalysts A and C are Pt/Rh on alumina; catalyst B contains Pt on alumina.

## RESULTS AND DISCUSSION

### *Influence of pressure*

Experiments were performed under nitrogen at  $525^\circ\text{C}$  with a total pressure varying from 0.1 to 5 MPa. Ponderal yields of the various cracking phases are given in Fig. 3 as a function of the pressure. Molar yields (in M% of butadiene injected) for the main components of the liquid phase are

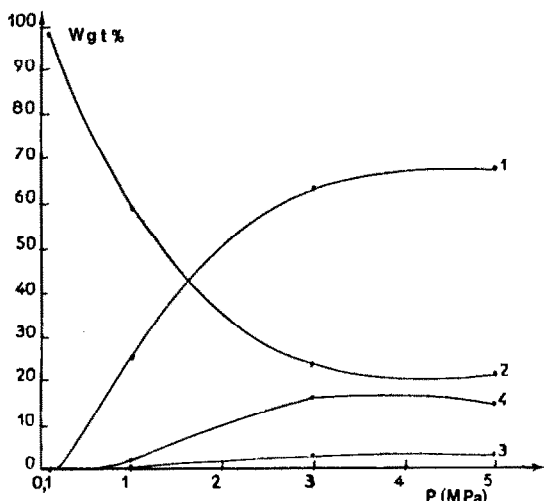


Fig. 3. Cracking yields (wt.%) as a function of pressure ( $T = 525^\circ\text{C}$ ): (1) liquid; (2) total gas; (3) solid; (4) gas except 1,3-butadiene.

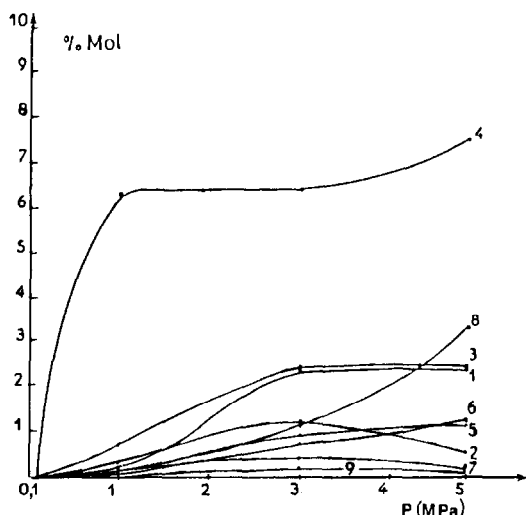


Fig. 4. Main liquid component yields (in M% of injected 1,3-butadiene) as a function of pressure ( $T = 525^{\circ}\text{C}$ ): (1) benzene; (2) cyclohexene; (3) toluene; (4) 4-vinylcyclohexene; (5) ethylbenzene; (6) *m*-xylene; (7) styrene; (8) *o*-xylene; (9) naphthalene.

shown in Fig. 4. 4-Vinylcyclohexene is the main primary product and its formation is favoured by increasing the pressure, mainly between 0.1 and 1 MPa.

This result confirms the Diels–Alder mechanism for the dimerisation of 1,3-butadiene, thermodynamically favoured by the pressure, and followed by the aromatisation reaction (1).

Gas analyses are shown in Fig. 5. As expected, the pressure increases the butadiene conversion, mainly to 4-vinylcyclohexene. The amount of hydrogen detected is always low. Ethane and propane yields increase slightly due to the hydrogenation of the short-chain unsaturated units by the  $\text{H}_2$  produced during the aromatisation of vinylcyclohexene. This reaction also explains the formation of butenes.

#### *Influence of the temperature*

The influence of the temperature was studied between  $350$  and  $575^{\circ}\text{C}$  under nitrogen with a total pressure of 3 MPa. Ponderal yields of the cracking phases are given in Fig. 6. It can be seen that a temperature increase has ultimately the same effect as a pressure increase. Liquid phase analysis is given in Fig. 7 in moles/100 moles of 1,3-butadiene injected. Between  $400$  and  $500^{\circ}\text{C}$ , the main product is 4-vinylcyclohexene.

#### *Influence of the catalysts*

Experiments with catalysts have been performed at  $525^{\circ}\text{C}$  under nitrogen with a pressure of 3 MPa. In each case, the mass of catalyst or inert solid

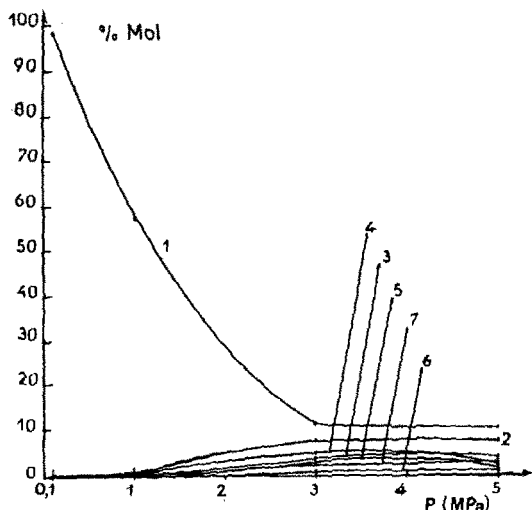


Fig. 5. Main gaseous component yields (M% of injected 1,3-butadiene) as a function of pressure ( $T = 525^{\circ}\text{C}$ ): (1) 1,3-butadiene; (2) methane; (3) ethene; (4) ethane; (5) propane; (6) *cis*- and *trans* 2-butene; (7) others.

material was 5.5 g. Table 1 shows that the presence of catalysts increases gas and solid formation at the expense of the liquids.

Analyses of the main cracking compounds in the liquid phase are given in Table 2 in g/100 g of liquid phase and in moles/100 moles of injected butadiene. It can be seen that in each case, the BTX yields obtained with

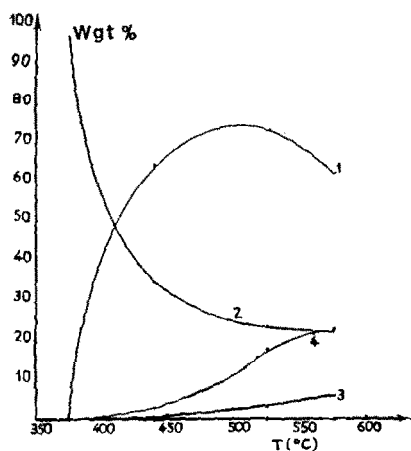


Fig. 6. Cracking yields (wt.%) as a function of temperature ( $P = 3\text{ MPa}$ ): (1) liquid; (2) total gas; (3) solid; (4) gas except 1,3-butadiene.

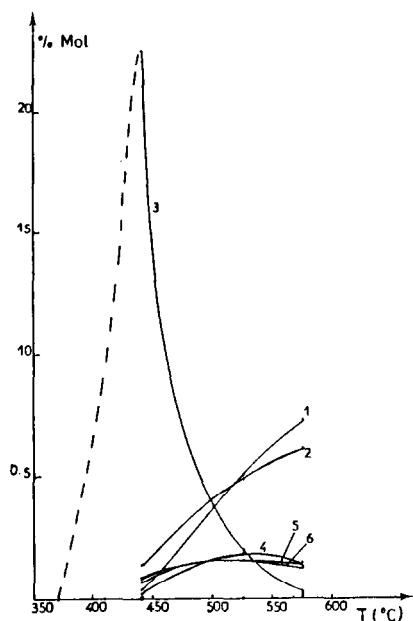


Fig. 7. Main liquid component yield (in M% of injected 1,3-butadiene) as a function of temperature ( $P = 3$  MPa): (1) benzene; (2) toluene; (3) 4-vinylcyclohexene; (4) *o*-xylene; (5) ethylbenzene; (6) *m*-xylene.

TABLE 1

Influence of catalyst on the cracking yields (wt.%) in inert atmosphere:  $P = 3$  MPa,  $T = 525^\circ\text{C}$

| Catalyst | A    | B    | C    | Inert |
|----------|------|------|------|-------|
| Liquid   | 50.6 | 55.2 | 51   | 70.1  |
| Gas      | 33   | 31.9 | 35.1 | 24.1  |
| Solid    | 16.5 | 9.4  | 12.0 | 3.1   |

TABLE 2

Influence of catalyst on the main cracking compounds in inert atmosphere:  $P = 3$  MPa,  $T = 525^\circ\text{C}$

| Catalyst           | A                |                  | B                |                  | C                |                  | Inert            |                  |
|--------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|------------------|
|                    | (1) <sup>a</sup> | (2) <sup>b</sup> | (1) <sup>a</sup> | (2) <sup>b</sup> | (1) <sup>a</sup> | (2) <sup>b</sup> | (1) <sup>a</sup> | (2) <sup>b</sup> |
| Benzene            | 10.1             | 3.5              | 5.6              | 2.1              | 9.4              | 3.3              | 10.4             | 5.1              |
| Cyclohexene        | 0.7              | 0.2              | 0.02             | 0.4              | 0.6              | 0.2              | 1.1              | 0.5              |
| Toluene            | 12.5             | 3.7              | 7.2              | 2.3              | 11               | 3.3              | 12               | 4.9              |
| <i>o</i> -Xylene   | 6.5              | 1.7              | 3.9              | 1.1              | 5.2              | 1.3              | 5                | 1.8              |
| <i>m</i> -Xylene   | 11.2             | 2.9              | 1.4              | 0.4              | 4.7              | 1.2              | 4.3              | 1.5              |
| 4-Vinylcyclohexene | 7.9              | 2.0              | 16.5             | 4.6              | 1.4              | 0.3              | 5.7              | 2                |
| Ethylbenzene       | 32.3             | 8.3              | 6.5              | 1.8              | 7.9              | 2.0              | 4.4              | 1.6              |
| Styrene            | 7.8              | 2.0              | 1.3              | 0.4              | 2.3              | 0.6              | 1.4              | 0.5              |
| Naphthalene        | 1.3              | 0.3              | 0.6              | 0.1              | 1.6              | 0.3              | 1                | 0.3              |

<sup>a</sup> (1) Ponderal composition of the liquid phase (in g/100 g of liquid phase).

<sup>b</sup> (2) Molar yield (in mol/100 mol of injected 1,3-butadiene).

TABLE 3  
Influence of hydrogen on the cracking yields (in wt.%) of 1,3-butadiene ( $P = 3$  MPa)

| Gas                 | N <sub>2</sub> | H <sub>2</sub> | N <sub>2</sub> | H <sub>2</sub> | N <sub>2</sub> | H <sub>2</sub> | H <sub>2</sub> | H <sub>2</sub> |
|---------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Catalyst            | A              | A              | B              | B              | inert          | inert          | C              | A              |
| Temperature<br>(°C) | 440            | 440            | 440            | 440            | 440            | 440            | 440            | 525            |
| Liquid              | 40.2           | 35.2           | 48             | 45.4           | 55.1           | 44.2           | 35.2           | 35.3           |
| Gas                 | 35.4           | 62             | 25.3           | 54.1           | 19.6           | 45.7           | 63.4           | 60.7           |
| Solid               | 17.5           | 2.4            | 9.2            | 2.3            | 7.8            | 4.2            | 0.7            | 6.4            |

catalyst are lower than without. Catalyst A leads to interesting yields in ethylbenzene and styrene showing an increasing aromatisation.

In order to inhibit carbon deposition on the catalyst, several experiments were performed at 440°C under hydrogen with a total pressure of 3 MPa. Cracking yields are shown in Table 3. As can be seen, hydrogen decreases the carbon formation but not to the benefit of the liquid phase.

The molar yields (moles/100 moles of injected butadiene) of the main cracking compounds of the liquid phase are given in Table 4. Combined use of hydrogen and catalyst increases the BTX yields; but this is mainly due to the exothermicity of the reaction in the presence of hydrogen leading to a temperature increase. Yields are to be compared with those obtained under nitrogen and without catalyst at higher temperature.

TABLE 4  
Influence of hydrogen on the yield of main liquid compounds (in moles/100 moles of injected 1,3-butadiene) ( $P = 3$  MPa)

| Gas                     | N <sub>2</sub> | H <sub>2</sub> | N <sub>2</sub> | H <sub>2</sub> | N <sub>2</sub> | H <sub>2</sub> | H <sub>2</sub> | H <sub>2</sub> |
|-------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Catalyst                | A              | A              | B              | B              | inert          | inert          | C              | A              |
| Temperature<br>(°C)     | 440            | 440            | 440            | 440            | 440            | 440            | 440            | 525            |
| Benzene                 | 1              | 11.7           | 0.3            | 15             | 0.3            | 7.4            | 11.9           | 16.4           |
| Cyclohexene             | 0.1            | —              | 0.4            | 0.05           | —              | 0.1            | —              | 0.4            |
| Toluene                 | 1.0            | 2.9            | 0.7            | 7              | 0.5            | 2.8            | 3.5            | 1.8            |
| 4-Vinylcyclo-<br>hexene | 3.4            | —              | 14.4           | 0.5            | 11.6           | 0.2            | —              | —              |
| Ethylbenzene            | 3.3            | 0.7            | 1.0            | 0.9            | 1.8            | 3.2            | 0.9            | 0.3            |
| <i>m</i> -Xylene        | 0.5            | 0.5            | 0.3            | 0.6            | 0.4            | 1.4            | 0.8            | 0.2            |
| Styrene                 | 0.4            | —              | 0.4            | —              | 0.1            | 0.07           | —              | —              |
| <i>o</i> -Xylene        | 0.7            | 0.3            | 0.4            | 0.6            | 0.3            | 0.8            | 0.3            | 0.1            |
| Indene                  | 0.07           | 0.2            | 0.2            | 0.1            | —              | 0.1            | 0.2            | 0.09           |
| Naphthalene             | 0.09           | 0.5            | 0.2            | 0.6            | 0.1            | 0.05           | 0.7            | —              |

## CONCLUSIONS

The results show that pressure plays an important role in the first step of 1,3-butadiene aromatisation, mainly from 0.1 to 3 MPa. At atmospheric pressure and 525 °C, the 1,3-butadiene does not crack; at the same temperature but below 1 MPa, 33% of the transformed butadiene is converted to 4-vinylcyclohexene. At lower temperature (440 °C) and under 3 MPa, the conversion yield is higher: 74% of the transformed butadiene is converted to 4-vinylcyclohexene. The catalysts used in this research are not efficient with respect to light aromatic hydrocarbon formation, especially because of the significant levels of carbon deposited on their active sites. The presence of hydrogen partly inhibits the carbon formation and favours the production of BTX. But this increasing yield is mainly due to the exothermicity of the reaction under hydrogen pressure. To optimise the BTX yields obtained by Diels–Alder reactions of the short chain olefins, we propose a three-step procedure based on our recent and previously obtained results:

1. Diels–Alder reaction of the olefins at relatively low temperature (450–500 °C) and pressure (1–3 MPa) in inert atmosphere.
2. Recycling of the gas phase containing the residual olefins.
3. Post-cracking of the liquid phase containing the cyclo-olefins such as 4-vinylcyclohexene, at slightly higher temperatures (~ 700 °C) at atmospheric pressure.

Our results have also demonstrated that under hydrogen pressure, with the conditions of rapid carbonisation occurring in the hydrolysis of coal, the part of the Diels–Alder reaction between the short chain olefins remains important in the formation of light aromatic hydrocarbons.

## ACKNOWLEDGEMENT

The authors wish to thank the Commission of the European Communities for financial assistance.

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