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Influence of pressure (100 Pa–100 Mpa) on the pyrolysis of an alkane at moderate temperature (603 K–723 K): Experiments and kinetic modeling

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ABSTRACT

Confined pyrolysis of *n*-octane was performed in a closed, constant-pressure gold reactor at pressure ranging 1 MPa–70 MPa, temperature between 603 K and 723 K and residence times from 1 h to 1 month. The main products of reaction are *n*-alkanes of molecular weight lower than *n*-octane and branched alkanes of molecular weight higher than *n*-octane. Alkenes are minor products. At moderate temperature (603 K–623 K) the conversion of *n*-octane increases with pressure up to a maximum and then decreases (at constant duration of pyrolysis). For higher temperature (723 K) the conversion increases continuously with increasing pressure. A mechanism consisting of 182 free-radical reactions is set up and used to model these experimental results (1–70 MPa) as well as those obtained in a previous study at very low concentration (100 Pa diluted in inert gas, total pressure 0.15 MPa). The agreement between the experimental data and simulation results is satisfactory in terms of product distribution and conversion of *n*-octane in a wide range of pressure (100 Pa to 70 MPa). Some mechanistic explanations concerning the effect of pressure are proposed.

1. Introduction

The pyrolysis of alkanes has been the focus of many studies for a very long time (e.g. [1–7]). The pyrolysis reactions also known as thermal cracking or thermal decomposition are involved in many sectors of chemistry: coal liquefaction (e.g. [8–10]), oil refining (e.g. [11–13]), oil evolution in petroleum reservoirs (e.g. [14–23]), jet-fuels stability for high Mach Number aircrafts [24–27], or deposition of pyrolytic carbon to produce Carbon/Carbon composites by a chemical vapor infiltration process [28–33]. These pyrolysis reactions are of great industrial and commercial importance. The pyrolysis of *n*-alkanes, especially at high pressures (several hundred MPa) has also been of interest to the petroleum geochemistry community. Indeed, laboratory experimentation of the thermal stability of petroleum combined with kinetic modelling is a major methodology aiming to understand the fate of petroleum in geological reservoirs (e.g. [34–42]).

The studies carried out so far focused on very narrow experimental conditions of temperature and/or pressure. The experiments performed at low pressure (about 100 kPa) showed that alkanes and olefins are generated in almost equal quantity [1,43,44]. On the other side very few olefins and notable amounts of alkanes are produced in experiments carried out at very high pressure [2,39,43,45–49]. Some authors also studied the influence of pressure on the *n*-alkane conversion. Fabuss et al. [43] gathered numerous results obtained in the range 0.1–100 MPa. They highlighted that pressure up to about 40 MPa increases the pyrolysis rate and pressure above 40 MPa inhibits pyrolysis. Similar conclusions were drawn by Behar and Vandenbroucke [39], and Yu and Eser [50]. Dominé [35] and Dominé et al. [37] focused on the effect of pressure on the products distribution by experimental and modelling studies. Mallinson et al. [51] also conducted a detailed kinetics study of the role of pressure in alkane pyrolysis.

In this study, we intend to establish the link between these various studies by trying to understand how changes in experimental conditions (pressure and temperature) influence the various processes and thus modify the selectivity to products and the conversion of *n*-octane.

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Table 1
Experimental: conditions of high pressure pyrolysis of *n*-octane.

Temperature	Pressure	Time
603 K	70 MPa	From 3 days to 1 month
603 K	10 MPa	From 3 days to 1 month
623 K	70 MPa	From 3 days to 1 week
623 K	10 MPa	From 3 days to 1 week
723 K	70 MPa	From 1 h to 3 h
723 K	1 MPa	From 1 h to 3 h

We chose octane as the reference alkane to carry out the study of the influence of experimental conditions on the alkane pyrolysis. Indeed its molecular size allows a rather wide range of smaller and larger products which are easy to analyze by Gas Chromatography.

This paper presents the experimental procedure and the pyrolysis results of octane at high pressure (1–70 MPa). From these results combined with those of a previous work [52] performed at low concentration (molar fraction 0.07%, partial pressure 100 Pa diluted in Argon – total pressure 0.15 MPa), a model of octane pyrolysis based on free radical reactions has been developed to account for experiments from low to high pressure.

2. Experimental set up at high pressure (1–70 MPa)

2.1. Sample

n-Octane (purity 99%) was obtained from Aldrich and used as received.

2.2. Confined pyrolysis procedure

Pyrolysis was carried out in gold cells (40 mm length, 5 mm i.d. and 0.5 mm thick). Gold tubes were sealed at one end then filled with 30 mg of sample under helium atmosphere (purity 99.9999%) to avoid the presence of oxygen, and then arc welded at the other end under a refrigerated nitrogen flow in order not to damage the hydrocarbons. The gold cells were loaded in stainless steel autoclaves pressurized at 1, 10 and 70 MPa, while temperature was set in the range 603–723 K, during 1 h to 1 month (Table 1). At the end of the pyrolysis, the autoclaves were rapidly (5 min) cooled to room temperature in a water heat exchanger so that cooling time was negligible relative to heating time. For each experimental condition, two or three samples were used for quantitation in order to check the reproducibility and one sample was used for products identification. Details of the confined pyrolysis procedure can be found in [53–56].

2.3. Identification of products

Gold cells were pierced, cut in pieces, placed into a vial containing hexane and extracted in an ultrasonic bath for 1 h. Compounds were identified by gas chromatography–mass spectrometry (HP 5890 Series II GC coupled to a HP 5971 mass spectrometer) using a 60 m DB-5 J & W Scientific, 0.25 mm i.d., 0.1 mm film, fused silica column. The temperature program was 333–433 K at 15 K/min followed by heating to 573 K at 3 K/min.

2.4. Quantitation of products

Gold cells were pierced in a vacuum line maintained at 523 K [57]. An aliquot fraction of 0.5 mL was sampled on-line and injected through a heated transfer line into a HP 5890 Series II GC with a 60 m DB-5 J & W Scientific, 0.32 mm i.d, 0.45 μm film and a fused silica column connected to a flame ionization detector. The temperature program was 273 K during 1 min followed by an increase of 6 K/min up to 573 K. The compounds were quantitated after calibration of the FID using commercially available standards.

3. Experimental results at high pressure (1–70 MPa)

3.1. Reaction products

An example of chromatogram of the reaction products is presented in Fig. 1.

The main reaction products are light *n*-alkanes (of molecular weight lower than that of *n*-octane): CH_4, C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12} and C_6H_{14}. At the bottom of these peaks, small peaks which are very difficult to precisely identify are observed. There are mainly alkenes and cycloalkanes.

The molar fractions of the products and *n*-octane obtained after pyrolysis in the different experimental conditions are presented in Supplementary material 1.

The heavy products (mainly C_{10}-C_{15}), in smaller quantity, are composed of branched alkanes. Regarding these compounds, identical series from 3 to 5 peaks can be seen, suggesting a similar mechanism of formation.

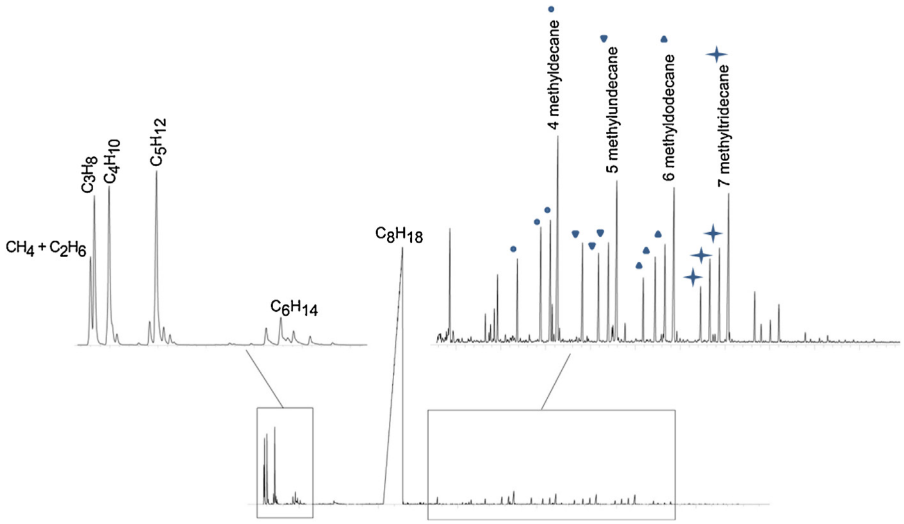

Fig. 1. Chromatogram obtained after pyrolysis of *n*-octane at 623 K, 70 MPa and 5 days. The compounds observed are typical of the octane pyrolysis obtained in this study. Compound identification by names or formulae. Unlabelled peaks are *iso*-isoalkanes isomers of the identified peaks. The very small peaks are alkenes and cycloalkanes.