

N°239 / OC / PC

TOPIC(s) : Biomass conversion / Industrial chemistry

## "Millisecond" reactor for green chemistry

### AUTHORS

Hugo CRUCHADE / INSTITUT DE CHIMIE DES MILIEUX ET MATÉRIAUX DE POITIERS, UMR 7285 CNRS, 4 RUE MICHEL BRUNET, BÂTIMENT B27, POITIERS CEDEX

Romain BEAUCHET / INSTITUT DE CHIMIE DES MILIEUX ET MATÉRIAUX DE POITIERS, UMR 7285 CNRS, 4 RUE MICHEL BRUNET, BÂTIMENT B27, POITIERS CEDEX

Yannick POUILLOUX / INSTITUT DE CHIMIE DES MILIEUX ET MATÉRIAUX DE POITIERS, UMR 7285 CNRS, 4 RUE MICHEL BRUNET, BÂTIMENT B27, POITIERS CEDEX

Ludovic PINARD / INSTITUT DE CHIMIE DES MILIEUX ET MATÉRIAUX DE POITIERS, UMR 7285 CNRS, 4 RUE MICHEL BRUNET, BÂTIMENT B27, POITIERS CEDEX

Corresponding author : Ludovic PINARD / ludovic.pinard@univ-poitiers.fr

### PURPOSE OF THE ABSTRACT

#### Introduction

The industrial cracking of hydrocarbons currently occurs through catalytic (CC) or steam cracking (SC) [1]. The C-C bond cleavage yields to: (i) a limited selectivity in valuable linear alpha-olefins ( $nC > 6$ ), (ii) a positive enthalpy (320 kJ/mol) that implies elevated reaction temperatures, hence high energy cost, and (iii) in the case of CC, a fast deactivation of the acid catalyst. Schmidt and coll. [2-3] proposed an alternative way to overcome this by cleaving the C-H bonds through an oxidative catalytic reaction, supplying enough energy to reach an auto-thermal state. Nevertheless, extremely low contact times (few ms) and homogeneous mix gas are required to avoid the auto-ignition of hydrocarbons. The oxidative cracking (OC) way, contrariwise to CC and SC processes, allows obtaining long chain olefins. This could be applied in bio-refinery on the liquid biomass cracking (vegetable oils); e.g. the OC of oleic acid should lead to very valuable compounds such as di- or olefinic- acids. The application of the Schmidt's process on vegetable oils requires discriminating between the proportion of thermal and catalytic cracking occurring inside a millisecond reactor. The OC of a series of model molecules (n-decane, n-dodecane, 1-decene and methyl decanoate) will be carried out in order to understand all the mechanisms involved. Only the results obtained from n-decane will be presented hereafter.

#### Experimental

The millisecond reactor is constituted of (1) a vaporization zone including a mass flow controller and an automotive injector allowing both to control the carbon to oxygen molar ratio (C/O) and to warrant an homogeneous feed gas composition, (2) a reaction area with an oven used to preheat the catalyst (280°C). The two ceramic monoliths (400 cpsi,  $v = 2.2 \text{ cm}^3$ ) were washcoated with 12 wt% gamma-alumina impregnated with (i) 2 molar% Rh or (ii) 1 molar% Pt. The catalyst temperature was recorded with a thermocouple in contact with its outlet. The n-decane transformation was carried out at a pressure of 0.14 MPa, C/O molar ratio of 1.3 and a contact time through the monolith of 29 ms. In the case of pyrolysis (Pyr) and catalytic pyrolysis (Cat-Pyr) of n-decane studies, the residence time was 700 ms, the air was replaced by nitrogen and the Rh-monolith was used as catalyst. The temperature was similar as the oxidative catalytic cracking (OCC) one (600°C).

#### Results and discussion

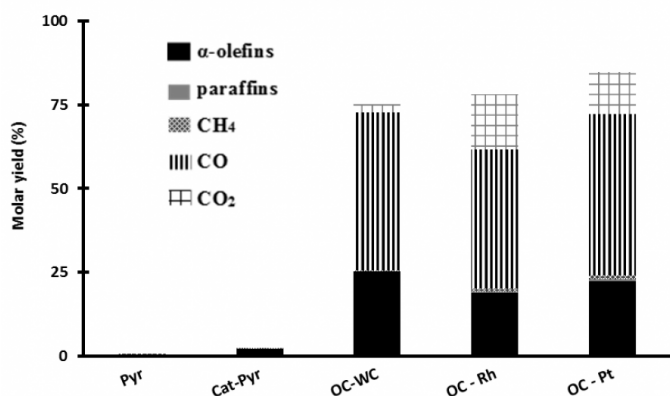
The thermal cracking conversion of n-decane with a long residence time (700 ms) at 600°C is only 0.5 % (fig.1). The cracking products are mainly alpha-olefins ranging up to 9 atoms without particular distribution; a non-selective distribution, (i.e. statistical) is due to the non-selective character of the thermal cracking. Moreover, the presence of Rh/Al<sub>2</sub>O<sub>3</sub> has no impact neither on the cracking yields or on the selectivity (fig.1). In the case of

OC, the preheating of feed gas at 280°C is enough to oxidize n-C10, that increases the temperature in the reaction area. Hence, the millisecond reactor is becoming auto-thermal. Without catalyst (OC-WC), the reaction occurs in gas phase, the temperature reached is 440°C. The n-decane OC produces (fig.1) CO<sub>2</sub> and CO, (added value product as syngas), and hydrocarbons, mostly alpha-olefins. In presence of a catalyst (Rh/Al<sub>2</sub>O<sub>3</sub>: OC-Rh or Pt/Al<sub>2</sub>O<sub>3</sub>: OC-Pt) the catalyst temperatures reach up to 600°C, the molar distribution of the cracking products (fig.2) is non-statistical and displays a maximum in the C<sub>2</sub> hydrocarbons family, that indicates a participation of metallic sites in the OCC mechanism.

#### Conclusion

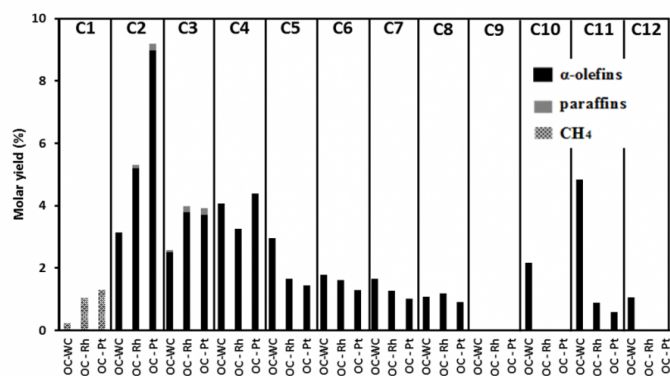
The OCC of hydrocarbons allows an auto-thermal formation of light olefins. In this process, the catalyst oxidizes one part of reactant releasing heat enough to cleave catalytically the C-C bond. These results are promising for ahead studies on the cracking of vegetable oils in order to obtain very valuable molecules such as the diacid compounds.

## FIGURES



**FIGURE 1**

Molar yields of reaction products obtained for the Pyr, Cat-Pyr and OC experiments.



**FIGURE 2**

Molar yields of cracking products obtained for the OC experiments.

## KEYWORDS

Vegetable oils transformation | Oxidative catalytic cracking | Auto-thermal process | Millisecond contact time

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