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Experimental and modelling study of methyl oleate pyrolysis between 500 and 650 °C

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RÉSUMÉ

Cet article décrit une étude expérimentale et mécanistique de la pyrolyse de l'oléate de méthyle dans un réacteur tubulaire à pression atmosphérique. La température de réaction varie entre 500 et 650°C. Les temps de passage étudiés sont 230, 350, 500 et 600 ms.
Le mécanisme radicalaire proposé rend compte qualitativement de toutes les espèces observées expérimentalement. Ce mécanisme donne un bon accord entre les valeurs expérimentales et simulées des fractions molaires des produits de la réaction de pyrolyse.

Mots-clé : oléate de méthyle, mécanisme, pyrolyse, réacteur tubulaire, modélisation cinétique.

ABSTRACT

This paper describes an experimental and modelling study of methyl oleate pyrolysis in a tubular flow reactor at atmospheric pressure. The reaction temperatures ranged from 500 to 650°C. The residence times were 230, 350, 500 and 600 ms.
The proposed radical mechanism describes qualitatively all experimental observed species. This mechanism displays a satisfactory agreement between experimental and simulated values of molar fractions of pyrolysis reaction products.

Key-words : methyl oleate, mechanism, pyrolysis, flow reactor, kinetic modelling.

INTRODUCTION

This work is a contribution to the non-alimentary upgrading of biomass. We studied the pyrolysis of methyl oleate (major rapeseed oil methyl ester) in order to obtain high added value molecules (alphaolefins in the cut C10 - C14 and mono-unsaturated ester in the cut C6:1 - C12:1). These molecules could be used as raw materials to produce biodegradable surfactants, detergents and lubricants.

I EXPERIMENTAL STUDY OF METHYL OLEATE PYROLYSIS BETWEEN 500°C AND 650°C

I.1 Experimental procedure

The experimental work was performed at atmospheric pressure in a tubular flow reactor (figure 1) [1-2].

I.1.1 Injection of methyl oleate and nitrogen

Methyl oleate and nitrogen were injected separately. Methyl oleate was injected by an isocratic pump (Spectra Physics type SP 8810). The flow rates of the pump were between 0.3 and 10 cm^3/min. Nitrogen (AIR LIQUIDE) was injected by a mass flow regulator.

I.1.2. Preheating and mixture

Methyl oleate and nitrogen were preheated separately in stainless steel tubes surrounded by a roll of heating resistors (Thermocoax). The diluent was preheated to 400°C and the mixture to 490°C.

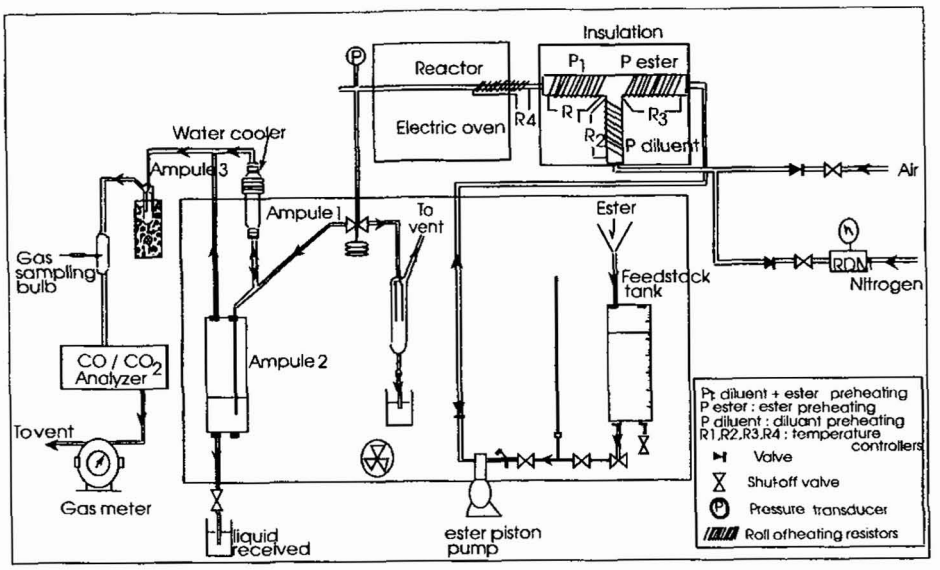

Figure 1 : Detailed scheme of the pyrolysis pilot [1,2].

1.1.3. Reactor

We used an electric oven (brand name : VECSTAR) where the temperature remained steady around the middle of the oven in a portion of 15 cm. The oven had its own regulator system.

The tubular flow reactor (length 52 cm, internal diameter 9.44 mm) was made of stainless steel and located in the furnace. The residence times in those conditions ranged from 230 to 600 ms.

A thermocouple placed in the centre of the reactor gave the effective temperature. A pressure controller situated at the outlet of the rector measured the pressure.

1.1.4.Trapping of products

At the reactor outlet, a shut-off valve allowed the passage of outlet products into the analysis circuit in order to do mass balances during the time of assessment (30 to