

# OXIDATION OF AROMATIC HYDROCARBON IN A LOW-PRESSURE PLASMA CATALYTIC FLUIDIZED-BED REACTOR

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## Abstract

The aim of the present work is the study of the selective oxidation of toluene. Experiments have been performed in a low-pressure (80 Pa) fluidized-bed of catalyst plasma reactor. Mass balance of reactions is determined by gas chromatography. Depending on the nature of the catalyst the oxidation of toluene leads to two kinds of products. The total destruction of aromatic molecule with formation of carbon oxides is obtained with a type N semi-conductor catalyst while high added value molecules (phenol, cresols, etc....) are formed when zeolites (mordenite or faujasite) are used in the fluidized-bed. Depending on the catalyst used, such a process can find applications to destruction of toxic molecules or the formation of high added value compounds under "limited temperature" conditions.

## Introduction

Thermal plasmas are very suitable procedures for cleaning up processes or for destruction of organic toxic materials because of the high temperature obtained in plasma reactors where all molecules are completely destroyed. However in some cases, the fragments of these molecules are recombined forming molecule with the same toxicity as the destroyed ones. So, waste treatment plasma process (as well as conventional process) must include a step for trapping the products. On the other hand, as the majority of chemical processes use heterogeneous catalysis, it is suitable to associate in the plasma process a catalyst in order to trap the products of the destruction and to make selective reactions. The association of a thermal plasma and a fluidized-bed of catalyst seems to be promising [1]. The objective of our work is the study of the oxidation reactions of aromatic hydrocarbon (toluene) in a low-pressure plasma fluidized-bed reactor. The use of low pressure allows the study of the reactivity of organic species because there is no heating by plasma. Depending on the nature of the catalyst the oxidation of toluene leads to the formation of higher added value molecules (phenol, cresols, etc..) or to carbon oxides. The plan of the paper is as follows. First, we will describe the experimental set-up and the characteristics of the particles used in the fluidized-bed. Then, we study the influence of the position of plasma with respect to the fluidized-bed on the reactivity of toluene. Finally, in order to show the influence of the nature of catalysts, we present the results obtained of conversion rate of toluene and yields of products formed, with the three kind of catalysts.

## Experimental set-up

The experimental set-up is shown in figure 1. The plasma is created in a Pyrex tube (30 mm diameter, 440 mm length) with particles of catalyst lie on a support. The power is supplied from a radio-frequency 13.56 MHz generator, through a solenoid-coil electrode which can be displaced along the reactor. The reactor is pumped down to a background pressure of 1 Pa by a mechanical pump. Toluene is evaporated when it is introduced into the reactor and its flow rate is controlled by a needle valve. The gas inlet is monitored by mass-flow meters and the pressure is measured by a capacitive manometer. The gaseous compounds are sampled by a dry vacuum pump and the liquid compounds are collected in a liquid-nitrogen trap.

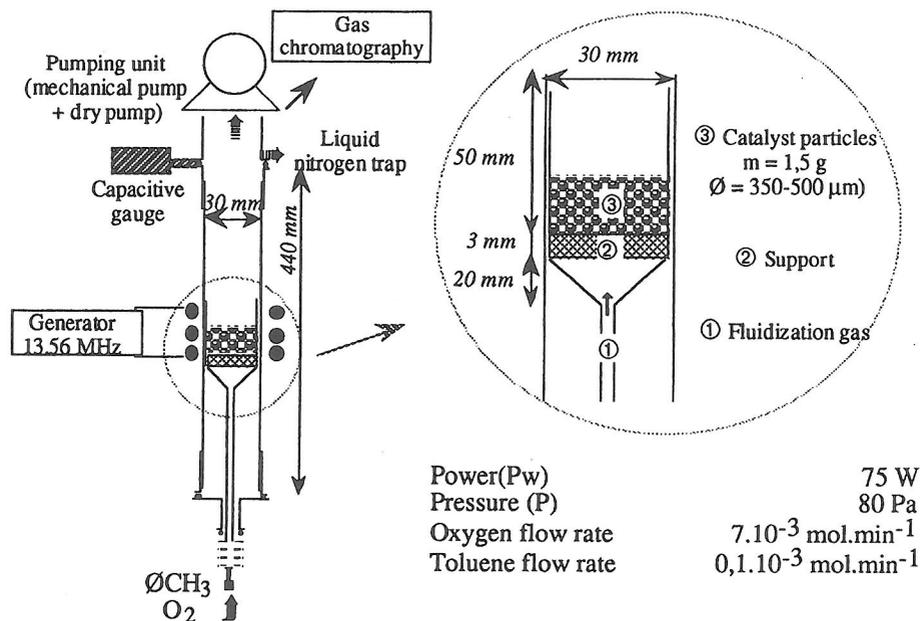


Figure 1: Experimental set-up and conditions

The catalysts used in the fluidized-bed are of two kinds: type N semiconductor oxides and zeolites. The first type of catalyst is NiO(4%)-WO<sub>3</sub>(25%) supported on alumina, can supply O<sub>2</sub><sup>-</sup> and O<sup>-</sup> ions [2]. The second one are zeolites (crystalline aluminosilicates) : mordenite ZM 760 and faujasite YNa, with specific properties (acidity, shape, nature of compensation cation, size) that can favor the oxidation mechanisms [3]. Some characteristics of these catalysts are summarized in table 1. Qualitative analysis of the gas and liquid products was performed by GC/MS whereas quantitative analyses have been done by gas chromatography [4]. In some cases, a thin film was obtained on the reactor wall. This film was analyzed by infrared spectroscopy.

Catalyst	Density	Surface area (m <sup>2</sup> .g <sup>-1</sup> )	Cation nature	Si/Al	
<i>Semiconductor</i>	NiO-WO <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	2	180		
<i>Zeolites</i>	Mordenite ZM760	0,5	330	H <sup>+</sup> (acid)	60
	Faujasite YNa	0,5	530	Na <sup>+</sup>	5

Table 1 : Characteristics of the catalysts used in the low-pressure fluidized-bed reactor

The conversion rate of toluene (C), the fraction of toluene converted in liquids (L) and in gaseous and in solid film (G+D) and the yields of the main products are defined as follows:

$$\text{Conversion rate of toluene } C = \frac{m\phi\text{CH}_3(i) - m\phi\text{CH}_3(f)}{m\phi\text{CH}_3(i)}$$

$$\text{liquid products } L = \frac{m \text{ liquids collected}}{m\phi\text{CH}_3(i)}$$

$$\text{Toluene converted in gaseous products and solid film } G+D = (1 - L)$$

$$\text{Yield of product } p \text{ } \text{Yield} = \frac{m_p}{m\phi\text{CH}_3 \text{ converted}}$$

## Results and discussion

Experimental results from toluene oxidation show the formation of a great number of gaseous liquid and solid compounds listed in table 2.

	Liquid compounds	Gaseous compounds	Film deposited on wall reactor
Oxygenated compounds	methanol water	CO, CO <sub>2</sub>	oxygenated aromatic structures
	phenol benzaldehyde benzyl alcohol cresols (o, m and p)		
Non oxygenated compounds	benzene diphenylethane	hydrogen methane acetylene ethylene ethane	

Table 2 : Main compounds products from toluene oxidation

## Influence of the plasma position

The nature of the products depends strongly on the position of the inductive electrode with respect to the fluidized bed. The configuration 1 (half of the electrode overlaps the fluidized bed) enhances the formation of liquid products with a low conversion rate of toluene. On the contrary with the configuration 2 there is a total conversion of toluene and formation of gaseous (especially CO<sub>x</sub>) and solid products (figure 2).

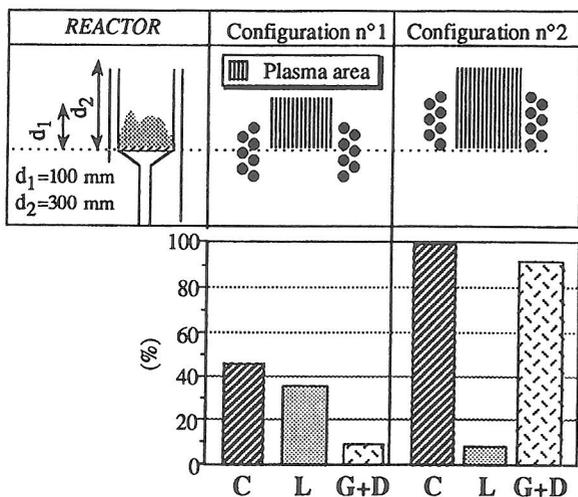


Figure 2 : Influence of plasma area on conversion of toluene

( $P = 80\text{ Pa}$  -  $P_w = 75\text{ W}$  -  
 $\text{ØCH}_3 = 1.10^{-3}\text{ mol.min}^{-1}$  -  
 $\text{O}_2 = 7.10^{-3}\text{ mol.min}^{-1}$  -  
 ZM760 (1,5 g) -  $t = 20\text{ min}$ )

Furthermore configuration n°1 leads to the formation of aromatic oxygen compounds (synthesis reactor) (figure 5). Configuration n°2 leads to the pyrolysis and total oxidation of toluene by reactions that open the aromatic ring. This configuration can be applied to the destruction of aromatic hydrocarbon processes (figure 3).

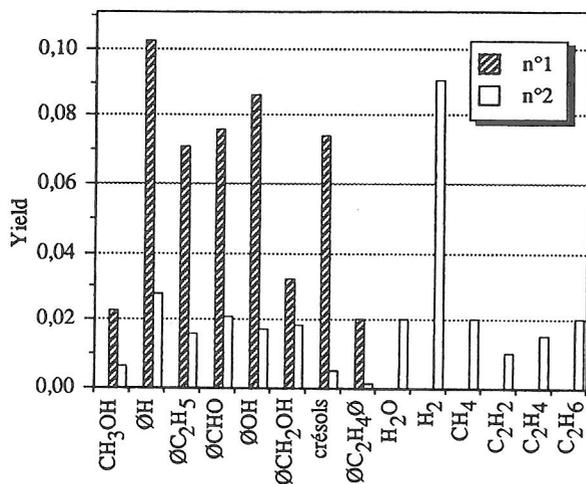


Figure 3 : Influence of plasma area on yields of products

( $P = 80\text{ Pa}$  -  $P_w = 75\text{ W}$  -  
 $\text{ØCH}_3 = 1.10^{-3}\text{ mol.min}^{-1}$  -  
 $\text{O}_2 = 7.10^{-3}\text{ mol.min}^{-1}$  -  
 ZM760 (1,5 g) -  $t = 20\text{ min}$ )

### Influence of the nature of catalysts

The influence of the nature of the catalyst used (NiO-WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>), YNa et ZM760) was carried out by comparing the results obtained without (reference) and with catalyst. The reactivity of toluene depends on the nature of the catalyst (table 3).

Catalyst	C (%)	L (%)	G+G (%)	Yield in CO
Reference	78	28	50	0,3
WO <sub>3</sub> /NiO	86	22	64	0,55
YNa	55	20	35	0,3
ZM760	45	36	9	0,2

Table 3 : Variation of conversion of toluene and yield in CO for the different catalysts  
( $P = 80 \text{ Pa}$  -  $P_w = 75 \text{ W}$  -  $\text{ØCH}_3 = 1.10^{-3} \text{ mol.min}^{-1}$  -  $\text{O}_2 = 7.10^{-3} \text{ mol.min}^{-1}$ )

The semiconductor oxide leads to a high conversion of toluene, producing high yields in CO. This result can be explained by the action of the labile oxygen ions which is particularly reactive [2,5], present in this type of catalyst (WO<sub>3</sub>). Zeolites yield aromatic oxidized compounds with low conversion rates of toluene. More specifically YNa yields more gaseous and solids products while ZM760 yields liquid products. The yield of CO remains low as in the reference experiments (20-30%). Furthermore the yield of liquid products is greater with ZM760 than with YNa and no inversion in the products distribution is observed (figure 4).

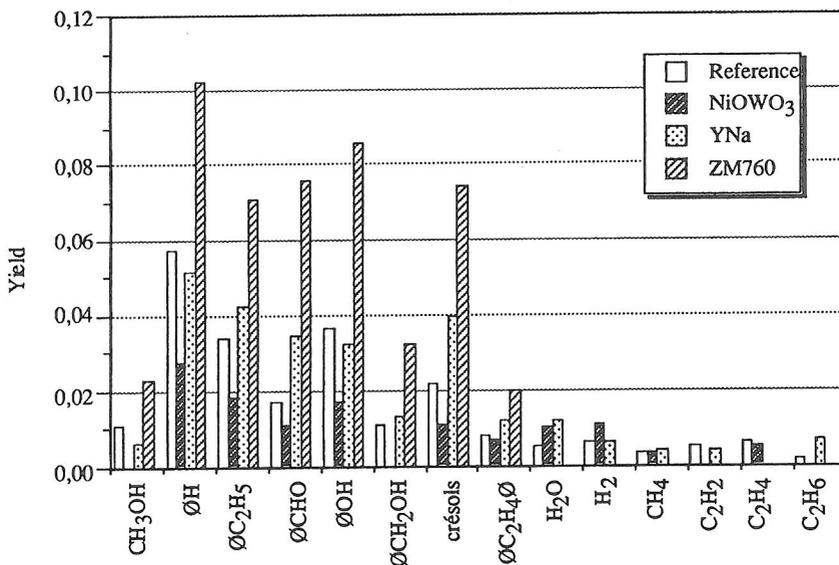


Figure 4: Variation of yields for the different catalysts used  
( $P = 80 \text{ Pa}$  -  $P_w = 75 \text{ W}$  -  $\text{ØCH}_3 = 1.10^{-3} \text{ mol.min}^{-1}$  -  $\text{O}_2 = 7.10^{-3} \text{ mol.min}^{-1}$ )

The difference in the distribution of the products with the zeolites depends on their respective chemical and structural properties. Concerning the chemical properties it is well known that ZM760 has a greater acidity than YNa and thus can supply OH radicals enhancing the formation of phenols. Concerning the structural properties even though the specific area of YNa is high (530 m<sup>2</sup>/g) as the lattice is tridimensional this area

decreases rapidly because the pores are obturated by the large molecules leading to the loss of the catalytic activity. In the case of ZM760 the lattice is bidimensional, so its specific area decreases slowly. After 20 min of work the two catalysts have comparable specific areas. The analysis of the compounds extracted from the catalysts after treatment by the plasma shows the presence of high molecular weight hydrocarbons resulting from the condensation of two or three molecules of toluene. The quantity of organic compound "trapped" in the catalysts represent 11% and 3% of the total mass of the catalysts for ZM760 and YNa respectively. X rays analysis of the catalysts show that their structure remains still crystalline after their treatment.

## Conclusion

Oxidation of toluene in low pressure plasma catalytic fluidized bed reactor pointed out the possibility to study its reactivity without any interference with thermal effects. In this work it was proofed out that it is possible to destroy aromatic hydrocarbons or to make high added value compounds with the use of catalysts. Under the same experimental conditions type n- semiconductor oxide catalysts ( $\text{WO}_3/\text{NiO}$ ) lead to the destruction of toluene while zeolites produce high added value hydrocarbons. The use of mordenite (ZM760) enhances the formation of liquid oxidized hydrocarbons while this of fujasite (YNa) leads to the formation of gaseous and solid products. In the future work the use of  $\text{WO}_3/\text{NiO}$  has to be investigated under thermal plasma conditions but also the effect of cations (copper or cobalt) that enhance the catalytic activity of zeolites [6].

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