

CRACKING OF HYDROCARBONS IN A PLASMA REACTOR WITH HIGH CONCENTRATION OF ACTIVATED HYDROGEN : INTERACTIONS H° / CH_3° RADICALS AND EFFECTS ON HYDROCARBONS CONVERSION

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Abstract

Cracking reactions of hydrocarbons are based on radical reactions at high temperature. An Argon Hydrogen plasma is able to introduce in the system very high temperature (about 8 000°C) and a high flow of hydrogen radicals, thanks to the hydrogen dissociation. The trouble is that such temperature is too high for chemical reactions. A spouted bed permits to quench this plasma allowing a good conservation of hydrogen radicals. The well mixing of these species with hydrocarbons, at an adequate temperature, permits to consider radical chemistry with a high concentration of active hydrogen.

INTRODUCTION

The treatment of heavy hydrocarbons is an important actual problem because of the arrival on the market of more and more heavy hydrocarbons whose physical and chemical properties are similar to classical vacuum residues. The chemistry of the treatment is built on the use of hydrogen. The difficulty is that hydrogen molecule, in his fundamental state, is a very bad reactant (long residence time, high temperature, high partial pressure...). In these terms, an effort has been done on the elaboration of catalyst intended for favouring energy transfer between hydrogen and hydrocarbons. This approach comes up against two main difficulties, which are the high content of sulphur and heavy metals (Cr,V) and the carbonization reactions that affect tremendously hydrotreatment catalysts.

A thermal plasma hydrocracking process at atmospheric pressure has been developed [1]. The plasma produces a high flow of hydrogen radicals and a spouted bed is used for the plasma quenching in order to avoid coke formation. The conjunction of the plasma and the spouted bed allows to work in a non equilibrium system where hydrogen radicals are at least 10^5 upper than in equilibrium conditions[2][3][4]. Under these conditions the cracking yield of a model hydrocarbon (n-C₁₆) and of a mixture n-C₁₆+Toluene is up to 80% for a residence time ranging from 0.2 to 0.3 second.

EXPERIMENTAL SET-UP

The experimental set-up is composed of three different zones (cf. figure 1) :

- The plasma source, producing hydrogen radicals,
- A spouted bed reactor, quenching the plasma and mixing the plasma species with hydrocarbons,
- An effluent analysis zone, allowing the process characterization thanks to a mass balance calculation.

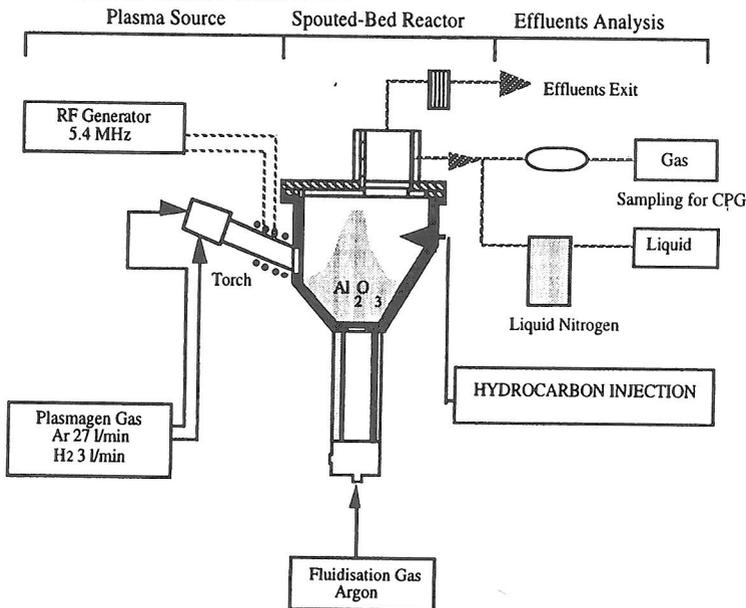


Fig. 1 : Experimental set-up

The plasma source

A high frequency current is applied with an inductor to a gas flow. The inductor is made of 4 water cooled copper coils. We use a double flow torch made in quartz which allows to introduce two independent gas. The double flow torch, supplied with up to 20% hydrogen in argon, is injected laterally in a two dimension spouted bed reactor. Our inductively coupled plasma (5.4 MHz) is characterized by an energy efficiency of 50%. The reactor is completely airtight and thermally insulated.

The atomic hydrogen is identified in the plasma by optical emission spectroscopy. The detection system is composed of a THR 1000 monochromator, an Optical Multichannel Analyser and an optical fiber of 1 mm diameter. The optical fiber is focused on the plasma centre, near the last coil. Two hydrogen atomic lines are observed : H_{α} ($3 \rightarrow 2$) at 6565 Å, and H_{β} ($4 \rightarrow 2$) at 4861 Å. Their intensities are relative to atomic hydrogen concentration.

The hydrogen radical flow increases with the plasma power. The average temperature of the plasma, measured with Boltzmann's method on argon and on hydrogen lines, is about 8000 K. This temperature corresponds to a total dissociation of hydrogen (reporting to complex chemical equilibrium calculations). Considering that hydrogen is not injected in the center of the plasma, we can estimate the dissociation degree of hydrogen as indicated in the table (1). Those values are in good agreement with Watanabe and coll calculations [7].

Applied plasma power (kW)	Ar = 29 l/min H ₂ = 1 l/min	Ar = 27 l/min H ₂ = 3 l/min
4	35	27
5	50	38
6	80	62

Table 1 : Hydrogen dissociation rate

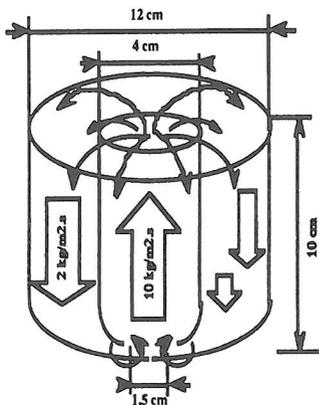
The spouted bed reactor

The reactor is a parallelepipedic alumino-silicate refractory reactor with a conical shaped base. The particles (usually alumina \varnothing 250-350 μm) are fluidized by argon. The particles fountain is able to quench the plasma jet in order to conserve a lot of hydrogen radicals at an adequate temperature for the hydrocarbons cracking.

The spouted bed has been hydrodynamically characterized by using Laser Doppler Anemometry (LDA). In order to measure the particles velocity, experiments were carried-out, at ambient temperature, on a same geometrical and size, but transparent reactor.

We have stored all particles velocity on several position of the fountain. In the center of the fountain, almost all particles are going up. When we move across the X axis, we begin to see more and more downward particles.

The mass flow is about +10 $\text{Kg}/\text{m}^2.\text{s}$ in the center of the fountain and about -2 $\text{Kg}/\text{m}^2.\text{s}$ on the edges (cf. figure 2). The mass flow, directly linked to the surface flow, is a very important parameter in regard to the quench and the hydrogen adsorption on particles. The residence time of a particle in the fountain is 2 seconds and in the bed, it is about 20 seconds.



-Particles: Alumina

Mass = 0.30 kg

\varnothing = 350 μm

-Fluidization gas : air

Gas velocity = 1.4 m/s

Particles velocity = 0.95 m/s

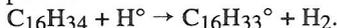
Fig. 2 : Working scheme of the fountain

A thermic map of the plasma spouted bed reactor has been done (cf. figure 3). The value of the quenching rate is about 5.10^5 K/s. This high value is obtained thanks to the good adequation of transport properties (mainly thermal conductivity and viscosity) of a spouted bed and of a plasma.

We demonstrate that recombination of these H radicals is directly correlated to the quenching rate. The results reported are confirmed by a kinetic program [5]. When the quenching rate increases, for a given temperature, the ratio H/H₂ increases. At 1000 K, thermodynamic calculations give an equilibrium between H and H₂ a mass ratio of $1.67 \cdot 10^{-9}$; with an experimentally measured quenching rate of $5 \cdot 10^5$ K/s, this ratio

Influence of hydrogen radicals on the cracking yield

The cracking yield of n-Hexadecane raises rapidly with the hydrogen plasma flow. This is explained thanks to the initiation reaction



Then β -scission reactions occur leading to α -olefins (ethylene, propylene, ...)[10][11].

Influence of hydrogen on carbonization

Hydrogen radicals have also an influence on carbonization reactions. This had been demonstrated by using a mixture of n-C₁₆ with methyl-naphthalene (cf. figure 4). Hydrogen can be introduced in the reactor either in the plasma, or in the fluidization gas.

Experimental parameters :

Plasma :
Ar + H₂ = 30 l/min
Power 4.16 kW

Fluidization :
Ar + H₂
Particles Al₂O₃ 450 g
Ø 350 µm

Residence time 0.3 s

Feedstock
nC₁₆ + 10% Me Naph

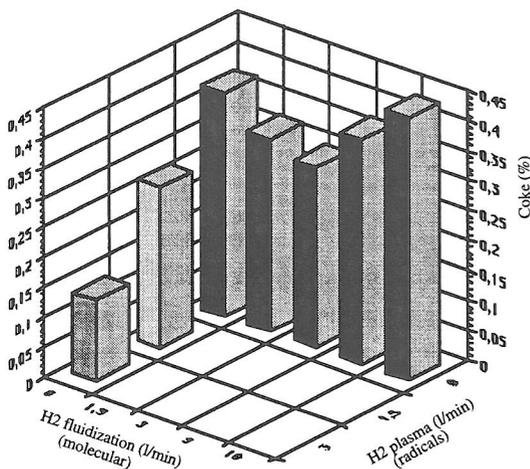


Fig. 4 : Influence of hydrogen on the carbonization

When hydrogen is introduced in the plasma, the formation of coke decreases rapidly with the hydrogen flow. When hydrogen is introduced in the fluidization gas, there is practically no effects on the coke. In other words, only hydrogen radicals, produced in the plasma, inhibit the coke formation. Thus, atomic hydrogen participate in promoting the scission of carbon-carbon bonds, increasing the conversion rate, and trap the incipient radicals to prevent retrograde reactions [8].

Competition atomic hydrogen / methyl radical

Experiments were carried out in the spouted bed reactor on the toluene. Cracking products (CH₄ -15% wt, C₂H₄ -10% wt, C₆H₆ -50% wt,...) allow to conclude that toluene is a methyl radical precursor. The question was : *Do methyl radical inhibits atomic hydrogen actions in the hydrocarbon cracking process ?* We have then studied the behaviour of several mixtures of toluene in n-C₁₆ at different cracking severity.

For weak cracking severity, the evolution of the mass ratio C₁₀/C₁₆ in the outlet products is a good sign of cracking, excluding the lack of precision of a mass balance. As it is shown on figure (5) and on table (3), toluene promote cracking.

Results pointed out an increase of the cracking rate of the n-C₁₆ (36→59% wt) with toluene. We noticed that this phenomenon was not observed in conventional thermic treatment (steam cracking) [9].

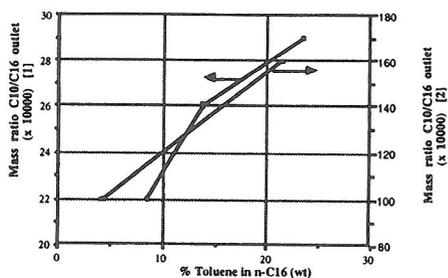


Fig. 5 : Influence of toluene on cracking

C_{10} = 1-Decene $C_{10}H_{20}$ product
 C_{16} = Hexadecane $C_{16}H_{34}$ remaining
 Plasma : Ar = 27 l/min, H_2 = 3 l/min
 Fluidization gas : Argon
 Particles Al_2O_3
 Feedstock flow nC₁₆ + Toluene
 Residence time 0.2 s
 Temperature at the injection point
 [1] T = 480°C
 [2] T = 530°C

Feed stock	Temperature (°C) at the injection point	Conversion rate of n-C ₁₆ (% wt)	Gas Yield (C ₁ - C ₄) (% wt)	Liquid Yield (C ₅ - C ₁₅) (% wt)
100% (wt) n-C ₁₆	580	36	22	14
90% (wt) n-C ₁₆ 10% (wt) Toluene	530	59	29.5	29.5
83% (wt) n-C ₁₆ 17% (wt) Toluene	530	58	45	13

Table 3 : Experimental results on the influence of toluene

CONCLUSION

The plasma spouted bed reactor allows the cracking of heavy hydrocarbons at atmospheric pressure with high yields. Hydrogen radicals, generated by the plasma and conserved thanks to the fluidized bed quench, permit the treatment of such hydrocarbons without using catalyst and without favouring carbonization reactions. In fact, the high concentration of hydrogen radical decreases the activation energy of cracking reactions (60→30 kcal/mol for the n-C₁₆), allowing an increase of the cracking rate. Atomic hydrogen is then able to promote the scission of strong carbon-carbon bonds such like $CH_3-C_6H_5$. Thus methyl radicals are created and enrich the system with active species.

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