STUDY OF A DESULFURIZATION PROCESS UNDER PLASMA CONDITIONS WITH Ar/H2 MIXTURE

M.N. Mohammedi, J.L. Leuenberger, J. Amouroux
Université Paris VI (Pierre et Marie Curie), École Nationale Supérieure de Chimie de Paris
Laboratoire de Génie des Procédés Plasmas. 11, rue Pierre et Marie Curie 75005 Paris, France

ABSTRACT

A co-processing of a fluidized spouted bed and an inductively coupled plasma had been developed for heavy hydrocarbon hydrocracking. High flow of hydrogen radicals is generated at high temperature (8000 K) by an Ar/H_2 plasma torch and the bed properties allow an important heat and mass transfer between plasma and particles, taking advantages of its transport properties. Hence a rapid quench of the plasma gas leads to an increase of hydrogen radical life-time.
The primary objective of this work is to understand the cleavage of C-S bond under these plasma conditions. To this end, thermodynamical calculations are done before experiments. Besides, preliminary experiments are carried out with different mixtures where n-hexadecane is always chosen as the model molecule in hydrocarbon hydrocracking, and sulphur compounds are added in small amounts (0-1% S mass). Compounds such as sulfides: dimethylsulfide, methyl-phenyl sulfide, a mercaptan:2-butanethiol and thiophen are currently studied.

INTRODUCTION

During these last years, investigations have been made on sulphur compound addition effects on various hydrocarbons such as methane (1975) [1], propane (1981) [2], heptane (1983), n-nonane (1985) [3], and in petroleum fraction such as naphta (1988) [4].
Sulphur compounds, like thiophenics have long been known to be fairly stable thermally and relatively unreactive. At this end, the behaviour of compounds such as thiophen, in n-hexadecane is investigated.
The researches are also directed towards extending these experiments to industrial feed stocks like gas-oil. The analytical results are obtained by off-line gas chromatography.
Moreover, the reactor parameters have to be taken into account, so as to point out the properties of the plasma phase ($H°$ and $CH_3°$ radicals) and those of the solid phase (Al_2O_3, CaO, $CaCO_3$).
In the same aim, a preliminary and predictive study had been realized on C-H-S-O system, and thermodynamical calculations permitted to determine the gas phase evolution: the stable species in function of the temperature, the pressure and the initial composition of the gas mixture, and then optimal reactor parameters.

1. PREDICTIVE CALCULATIONS

1.1. Thermodynamical evolution of the gas phase

Thermodynamic calculations for C-H-S-O system give information about stable species in function of temperature, pressure and initial composition of the gas mixture. Moreover,

these calculations lead to the prediction of optimal reactor parameters towards the distribution of molecules in the gas phase at the equilibrium state.
The principle of calculations is based on the Gibbs free energy minimization of the studied mixture using a second order Taylor method [5] . The calculation parameters are:
- thermodynamical parameters: pressure, temperature and free enthalpy versus temperature,
- different species considered at the equilibrium (molecules, atoms, ions, radicals),
- initial composition of the chemical mixture. Thermochemical data are taken from Janaf tables [6].
The computational program can only consider homogeneous phase cases. So, phenomena envolved in solid phase interaction could not be taken into account. Besides, this method does not predict the kinetic evolution of the physicochemical system.

In order to study the desulfurization of sulphur containing hydrocarbons, a first simulation was made. It is intended to represent the decomposition of an average petroleum section (C:H:O:S = 1 : 1.438 : 3.10^{-3} : $1.7.10^{-2}$ [7]. This result shows the important role of temperature and initial composition in C-S bond cleavage.

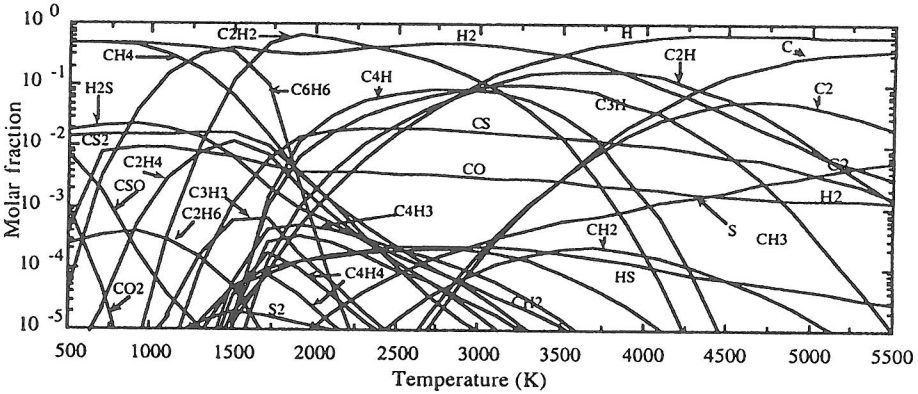


Figure 1: Complex equilibrium of the system: C:H:O:S = 1 : 1.438 : 3.10^{-3} : $1.7.10^{-2}$ at P=1atm·

The major products obtained (fig.1) are light hydrocarbons (CH_4, C_2H_2..), aromatic : hydrocarbons (C_6H_6), and sulfur molecules such as H_2S and CS_2. We observed that the effect of hydrogen addition (fig.2) is to eliminate progressively sulphure from hydrocarbons chains by formation of hydrogen sulfide which can easily be trapped by inert solids. The decomposition of sulfide hytdrocarbons must be carried out at temperatures under 2000 K, because of the growth of their stability with temperature elevation.

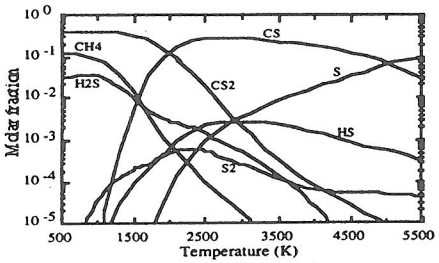


Figure 2: Complex equilibrium of the system: C:H:S = 4 : 4 :1, at P=1atm

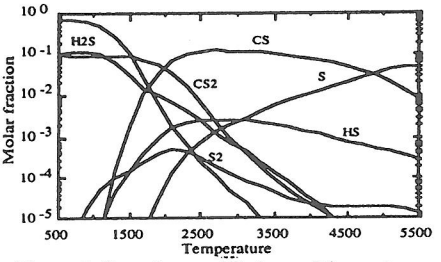


Figure 3: Complex equilibrium of the system: C:H:S = 4 : 12 :1, at P=1atm

Besides, the increase of oxygen amount in those systems leads to the apparition of toxic molecules such as SO_2, CSO and CO.

1.2. Thermodynamical study of the heterogeneous phase

One of the main objectives of this study is using a solid phase in the plasma post-discharge is to keep toxic molecules level in gas effluents under the ppm value. The toxic elements such as H_2S can be eliminated from the gas phase by trapping on solid particles and producing an inert solid [10]. The possibility of using alkaline earth oxides in such heterogeneous systems was demonstrated by means of free energy diagram of sulphur compounds (fig.4).

This diagram represents the thermodynamical stability of solids versus temperature and it suggests that using a spouted bed of alkaline earth oxide, like calcium oxide, seems to be suitable for trapping toxic sulphur containing gas by calcium sulfide formation. This can be possible at temperature up to 1170 K where calcium dioxide is able to react with toxic gases.

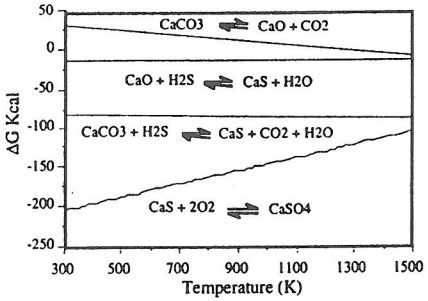


Figure 4: Free energy of different heterogeneous reactions versus temperature

2. EXPERIMENTS AND RESULTS

2.1. Experimental equipment

The reactor [8] is composed of a double-flow inductively coupled plasma torch working with an argon-hydrogen mixture. The torch injects the plasma laterally in the bed. The bed is a parallelepipedical refractory reactor with a regime of a jet spouted bed, where

particles - Al_2O_3, $CaCO_3$ or CaO - (250-350 μm) are fluidized by argon or hydrogen. The formed particle fountain divided the bed in two parts :
-the region in front of the plasma with temperatures in the range of 2500-1800 K,
-and the region behind the fountain with temperatures in the range of 700-1100 K.
The hydrocarbon feed stocks are injected in the latter region.

2.2. Results

The decomposition of n-hexadecane was investigated in the presence and absence of sulphur compounds which are introduced into the reaction system together with the feed. The purpose of this work is to study the influence of dimethyl sulfide, 2- butanethiol and methyl-phenyl sulfide on the conversion rate of n-hexadecane and on yields of products. Hydrogen sulfide produced is measured for each experiment by way of tube gas (Prolabo). The bed particles used are alumina particles (350μm). All sulphur compounds are added in the mixture at the same content: 1% mass of sulfur, in order to achieve comparable experiments. The hydrocarbon composition of gaseous and liquid product mixtures was determined by gas chromatography.
The qualitative and quantitative composition of the sulfur products are still not be possible at this time for analytical problems, nevertheless their effects on n-hexadecane decomposition are observed.

2.2.1. Products analysis

Gaseous products are analyzed by gas chromatography (Girdel 30, flame ionization) with ST104 column, and liquid ones by Shimadzu GC-9A chromatograph (flame ionization) with an SE 30 non polar column. Carbon black quantification is done thanks to reflectance measurements on normalized filters.

2.2.2. Mass balance and conversion rate

The mass balance is realized for gases and liquids. Analysis lead to mass balance in term of conversion as follows:
Conversion C (% mass) = mass flow n-C_{16} initial/mass flow n-C_{16} after reaction
Two samples are taken on the effluent gas: one in a glass gas sampling bulb (for gases C_1-C_4) and an other one in a liquid nitrogen trap (for liquid compounds C_5-C_{16}).

2.2.3. Experimental conditions:

Pressure: 1 atm, power : 4.16 kW, plasmagen gases: argon and hydrogen : 27l/min and 3l/min respectively, fluidization gas: argon: 42.9 l/min, total hydrocarbon flow: 0.4 kg/h, particles used: alumina 350 μm

2.2.4. Cracking of n-hexadecane

Previous works on n-hexadecane hydropyrolysis in plasma spouted bed reactor at atmospheric pressure and realized in the laboratory are summarized in the following conclusions:

- linear light α–olefins are principally obtained where ethylen and propylen are the main products,
- the carbon black formation can be neglected,
- the residence time is very short about 0.3 sec,
- n-hexadecane conversion rate increases while hydrogen flow increases [9],

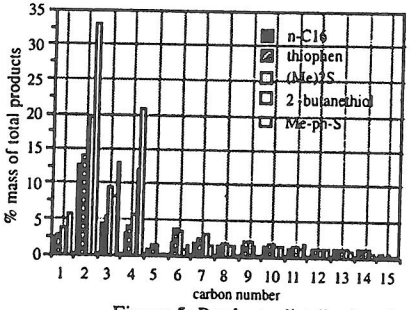
-hydrogen radicals produced by the plasma and quenched by the fluidized bed are involved in radical reaction processes, especially in initiation ones.
Under these conditions, at 973 K, with a residence time of 0.3 second, the cracking yield obtained is 37.4 % (wt). The major products are ethylen (33.45%), propylen (11.81%) and CH_4 (6.8%). Olefins represents about 90 % (wt) of the cracking products, and the coke less than 0.5 % (wt).

2.2.5. Effects of sulphur compounds on n-hexadecane cracking
The addition of sulphur compounds leads to an increase of gas and n-hexadecane conversion rate (table 1). Experimental conditions are on the whole similar, except for the fourth experiment (me-ph-sulfide) where the temperature is higher and the process is more a thermal one, but on the whole the conversion rate increase by 8 % for thiophen addition, 18 % for dimethyl sulfide and 2-butanethiol. Hydrocarbon product (without sulphurs) distribution is not really affected in these operating conditions in terms of quality, nevertheless, an increase of olefins of 2 % is observed (fig.5). Besides, C_2H_4 and C_2H_4 decrease while an increase of C_4H_6 can be noted.
Hydrogen sulfide amount for thiophen mixture is the lowest one (5ppm) because this compound is thermally stable and relatively unreactive. These properties have been attributed to its conjugated structure which allows the free electron to be largely delocalized.
The highest value is for 2-butanethiol mixture (140 ppm), and for sulfides: dimethyl and methyl-phenyl sulfide, hydrogen sulfide emission is at about the same.

Compounds added to n-hexadecane (1%S wt)	T_b (K) (bed temperature)	T_{inj} (K) (injector temperature)	% Gases	Conversion rate (%)	Hydrogen sulphur (ppm)
n-hexadecane	973	483	62	37.4	0
Thiophen	993	803	58	45.2	5
(Me)2S	993	803	67	55.3	60
2-Butanethiol	1028	872	79	55.4	140
Me-ph-S	1123	871	88	84.3	65

Table 1: sulphur compound effects

These results suggest that under plasma conditions sulphur compounds decomposition leads to radical production such as $CH_3°$, H°, HS° and Φ° which influence the course of radical reactions.



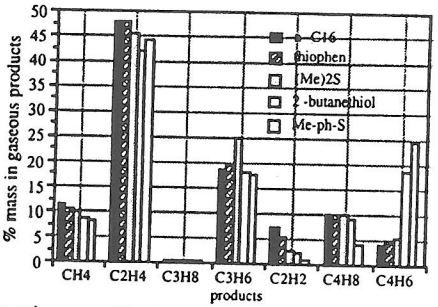
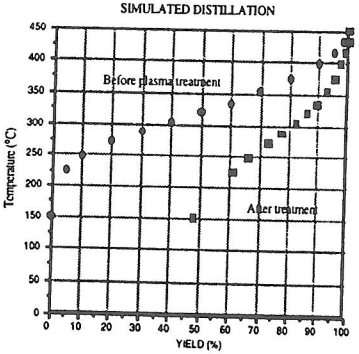


Figure 5: Products distribution for different mixtures with n-hexadecane (1% S)

2.2.6. Cracking of gasoline feedstock

The behaviour of a classical industrial feedstock (<150-450°C>; S=1.5 % wt) has been studied in the plasma spouted bed reactor. This oil product was characterized before and after the treatment (fig. 6).



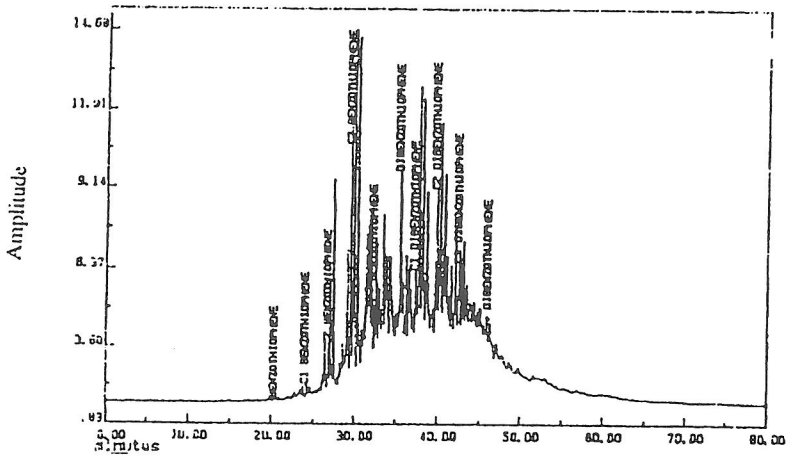
Experimental parameters :
Pressure: 1 atm
Plasma : Ar_{ax} = 15 l/min
Ar_{tg} = 12 l/min
H_{2tg} = 3 l/min
Power : 4.16 kW
Fluidization: argon = 39 l/min
Particles : Al_2O_3 :450 g , Ø= 350 µm
Feedstock: Gas-oil (S=1.5 % wt)
Flow : 384 g/h
Residence time : 0.3 s
Temperature: 740 °C

Figure 6 : Results of gasoline hydropyrolysis

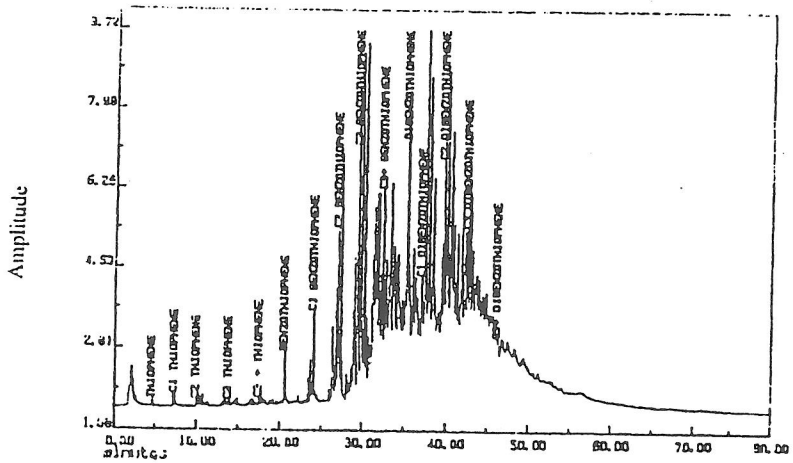
The effect of this treatment is to reduce heavy hydrocarbons (>300°C) from 60 to 18%, while conserving the middle product (<150-300°C>) up to 40%.
Sulphur compounds of the considered petroleum fraction have also been analyzed before and after plasma treatment on SPB sulfur column (Supelco) with chemiluminescence detector (fig.7). The preliminary observations were the followings:
- presence of sulphur compounds in the gas-oil : aliphatics and cyclics,
- hydrogen sulphur emission during plasma treatment, testifying to C-S bond cleavage,
- reduction of mercaptans and sulfides amounts,
- desalkylation of substituted benzothiophen,
- thiophen production after treatment which is testimony to ring opening.

Alkylated sulphur in gasoline feedstock are sources of $CH_3°$ radicals which have an effective influence on reactions occuring during hydrocarbon plasma pyrolysis. This is

validated by the increasing of the conversion rate in case of aliphatic hydrocarbons such as n-hexadecane.



Before plasma treatment



After plasma treatment

Figure 8 : Chromatograms before and after plasma treatment of gasoline feedstock (1.5% S)
(same operating conditions)
SPB sulfur column / chemiluminescence detector / Sievers

CONCLUSION

Sulphur compounds under plasma conditions, introduced into the reaction system together with the hydrocarbon injected, influence the rate of decomposition and the selectivity especially in terms of coke precursors in hydropyrolysis of hydrocarbons. Compared to the pure n-hexadecane, the decomposition rate increases by 8 to 18% depending on the nature of added sulphur compounds . In case of gasoline feed-stock, a desalkylation of substituted sulphur compounds and a ring opening in aromatic ones are observed.

ACKNOWLEDGEMENT

This research is supported by l'Institut Français du Pétrole, Elf Antar France, Elf Atochem, Total, Electricité de France and the CNRS Pirsem.

LITERATURE CITED

[1] A. Szymansky and A. Podgorsky, *Z. Phys. Chemie*, Lieipzig. 256, 4, S.765-769, 1975.
[2] D.L. Trimm and C.J.Turner, *J. Chem. Tech. Biotech.*. **31**, 285-289, 1981.
[3] D. Depeyre, C. Flicoteaux, *Ind. Eng. Chem. Process. Des. Dev.* 24, 920-924, 1985.
[4] D. Sahu and D. Kunzru, *Can. J. Chem. Eng.* vol 66, Oct 1988.
[5] J. Amouroux, D. Rapakoulias, *Ann. Chim.* 1, 227, 1976.
[6] Janaf Thermochemical Tables, *American Chemical Society.*
[7] B. Bertin, *Pétrole et Techniques.* N° 360, novembre-décembre 1990.
[8] S. Al Ayoubi, M.N. Mohammedi, J.L. Leuenberger, E.Francke, MF.Gonnord and J. Amouroux.*3rd European Congress on Thermal Plasma Processes*, Aachen, Germany, 1994.
[9] J.L. Leuenberger, M.N. Mohammedi, E. Francke and J. Amouroux. *Fluidization VIII — International Symposium of the Engineering Foundation*, 14-19 Mai 1995, Tours. 1995.
[10] Y. Liu et al, Preprints of Papers Presented at the *207th ACS National Meeting*, San Diego, CA, March, 13-17, 1994.