

DESULFURIZATION STUDY OF HYDROCARBON MOLECULES BY PLASMA PROCESS FOR GASOIL APPLICATIONS

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ABSTRACT

During these last years, many investigations have been made on sulphur elimination processes from hydrocarbon feedstocks because of environmental regulations which are more and more strict. This is a study on a plasma process dedicated to heavy hydrocarbon hydrotreatment and hazardous substances removing such as sulphur compounds. It is a co-processing of a fluidized spouted bed and an inductively coupled plasma working at atmospheric pressure. A high flow of hydrogen radicals is generated and a rapid quench of the plasma leads to an increase of hydrogen radical life-time and promotes chemical reactions of desulfurization at low temperature (700-900 K).

The primary objective of this work is to understand the cleavage of C-S bond under these plasma conditions. To this end, thermodynamic calculations are done and preliminary experiments are carried out with different mixtures where n-hexadecane is chosen as the model molecule in hydrocarbon hydrocracking, and sulphur compounds are added in small amounts (0-1 % S wt). Compounds such as dimethyl sulphide, 2-butanethiol, benzothiophene and thiophene are currently studied. The influence of CH_3° , H° , HS° and PhS° ($\text{C}_6\text{H}_5\text{S}^\circ$) is also considered.

INTRODUCTION

The development of upgrading processes in order to convert heavy feeds to lower boiling products, have to take into account the presence of components which make processing difficult, such as sulphur compounds. Besides, one of the operational problems of upgrading heavy feeds is the formation of undesirable high amounts of coke, which represent losses in hydrocarbonaceous materials and also need a costly separation step⁽¹⁾.

The development of such processes requires improvement of certain properties, especially H/C ratio. This is equivalent to adding hydrogen or rejecting carbon. For this reason, considerable attention is given to hydrogen addition technologies (hydrocracking) as opposed to carbon rejection technologies (thermal processes).

It has been revealed that hydrogen plays an important role in the activation and control of conversion of heavy feeds into marketable products^(2,3). However, high conversion of heavy feeds into distillate products require an efficient hydrogen activation, which can be promoted by adding a suitable catalysts. Nowadays many new and hydrotreatment catalysts are entering the market and their evaluation in terms of activity and stability is the subject of many recent works⁽⁴⁾. However, their use presents also inconvenients which are mainly reliable to deactivation phenomenon - due to the coke deposition and sintering of the active sites^(5,6) - and also to the high cost of the active metal species.

Our approach in this paper is to present briefly a new upgrading thermal inductively coupled plasma process working under atmospheric pressure and dedicated to heavy hydrocarbon hydrocracking. 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 coupling of the plasma and the spouted bed provides a non equilibrium system where hydrogen radicals amounts are 1000 times greater than those in an equilibrium system⁽⁷⁾. The use of such a process seems to be suitable since the high temperature and the high flow of radicals provide high efficiency of molecule decomposition such as sulphur compounds. In fact, plasma may operate by providing a source of hydrogen radicals through the dissociation of molecular hydrogen and then these radicals can promote the bond cleavage reactions.

Since many years, investigations have been made on sulphur compound addition effects on various hydrocarbons such as methane⁽⁸⁾, propane⁽⁹⁾, heptane, n-nonane⁽¹⁰⁾, and in petroleum fractions such as naphtha⁽¹¹⁾. Sulphur compounds, like thiophenics have long been known to be fairly stable thermally and relatively unreactive. At this end, the behaviours of compounds such as thiophene, n-hexadecane is investigated in this paper. The studies 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 thermodynamic calculations permitted to determine the gas phase evolution: the stable species versus the temperature, the pressure and the initial composition of the gas mixture, and then optimal reactor parameters.

PREDICTIVE CALCULATIONS

Thermodynamic 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⁽¹²⁾.

The calculation parameters are:

- thermodynamic 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 (13).

The computational program can only consider homogeneous phase cases. So, phenomena involved 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 ($C/H/O/S = 1/1.4383.10^3/3.10^{-3}/1.7.10^{-2}$) (14). This result shows the important role of temperature and initial composition in C-S bond cleavage.

The major products obtained (fig.1) are light hydrocarbons (CH_4 , C_2H_2 ..), aromatic hydrocarbons (C_6H_6), and sulphide molecules such as H_2S and CS_2 . We observed that the effect of hydrogen addition (fig.2) is to eliminate progressively sulphur from hydrocarbon chains by formation of hydrogen sulphide which can easily be trapped by inert solids. The decomposition of sulphide hydrocarbons must be carried out at temperatures under 2000 K, because of the growth of their stability with temperature elevation. Besides, the increase of oxygen amount in those systems leads to the apparition of toxic molecules such as SO_2 , CSO and CO (fig.3).

Thermodynamic study of the heterogeneous phase. One of the main objectives of this study in 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 (15). 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 sulphide formation. These can be possible at temperature up to 1170 K where calcium dioxide is able to react with toxic gases.

EXPERIMENTS AND RESULTS

Experimental equipment. The reactor (fig. 5) is composed of a double-flow inductively coupled plasma torch made of quartz and working with an argon-hydrogen mixture. The inductor is made of four water cooled copper coils. The double flow torch, supplied with up to 20% hydrogen in argon, is injected laterally in a two dimension spouted bed reactor. The inductively coupled plasma (5.4 MHz, 18 kW) is characterized by a global efficiency of 50%. The bed is a parallelepipedical refractory reactor with a regime of a jet spouted bed (16), 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 feedstocks are injected in the latter region.

Hydrocracking experiments. 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 sulphide, 2-butanethiol and methyl-phenyl sulphide on the conversion rate of n-hexadecane and on yields of products. Hydrogen sulphide produced is measured for each experiment by way of tube gas (Prolabo). The bed particles used are alumina particles (350 μm). All sulphur compounds are added in the mixture at the same content: 1 % wt of sulphur, 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 sulphur products are still not possible at this time for analytical problems, nevertheless their effects on n-hexadecane decomposition are observed. Gaseous products are analysed by gas chromatography (Girdel 30, flame ionization) with ST104 column, and liquid ones by Shimadzu GC-9A chromatographe (flame ionization) with an SE 30 non polar column. Carbon black quantification is done thanks to reflectance measurements on normalized filters.

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}) (fig.5).

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 .

Hydrocracking of n-hexadecane. Previous works on n-hexadecane hydropropylolysis 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 ethylene and propylene are the major products,
- the carbon black formation can be neglected,

— the residence time is very short about 0.3 seconds,
— n-hexadecane conversion rate increases while hydrogen flow increases,
— 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 ethylene (33.45 %), propylene (11.81 %) and CH₄ (6.8 %). Olefins represents about 90 % (wt) of the cracking products, and the coke less than 0.5 % (wt).

Effects of sulphur compounds on n-hexadecane hydrocracking. 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-sulphide) where the temperature is higher and the process is more a thermal one, but on the whole the conversion rate increase by 8 % for thiophene addition, 18 % for dimethyl sulphide and 2-butanethiol. The 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.6). Besides, C₂H₄ and C₂H₂ decrease while an increase of C₄H₆ can be noted.

Hydrogen sulphide amount for thiophene mixture is the lowest one (5 ppm) 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 sulphides : dimethylsulphide and methyl-phenyl sulphide, hydrogen sulphide emission is at about the same.

These results suggest that under plasma conditions, the cleavage of hydrocarbons is intimately related to the appearance of highly reactive light radicals such as CH₃[•], H[•], HS[•] and PhS[•] and which influence the course of radical reactions and the rate of hydrogen transfer is one of the main factors to be considered in mechanism understanding. Thus, the fact that thiols have the ability of accelerating H-transfer reaction by a factor of 200⁽¹⁷⁾ might be explain at least in part the increase of n-hexadecane conversion for 2-butanethiol mixture.

Cracking of gas oil 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. 7).

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⁽¹⁸⁾ on SPB sulfur column (Supelco) with chemiluminescence detector. The preliminary observations were the following:

- 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 sulphides amounts,
- dealkylation of substituted benzothiophene,
- thiophene production after treatment which is testimony to ring opening.

Alkylated sulphur compounds in gasoline feedstock are sources of CH₃[•] radicals which have an effective influence on reactions occurring during hydrocarbon plasma pyrolysis. This is validated by the increasing of the conversion rate in case of aliphatic hydrocarbons such as n-hexadecane.

CONCLUSION

Sulphur compounds under plasma conditions, introduced into the reaction system together with the feed, catalyses the rate of n-hexadecane decomposition and influence the selectivity especially in terms of coke precursors during hydrocracking. Compared to the pure n-hexadecane, the decomposition rate increases by 8 to 18% depending on the nature of added sulphur compounds which are effective H-transfer catalysts and improve the yield of α -olefins. The decomposition increase as the amount of thyl radicals is increased. In case of gas oil feedstock, a dealkylation of substituted sulphur compounds and ring opening in aromatic ones are observed

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| Compounds added to n-hexadecane (1% S wt) | T _b (K) (bed temperature) | T _{inj} (K) (injector temperature) | % Gases | Conversion rate (%) | Hydrogen sulfur (ppm) |
|---|--------------------------------------|---|---------|---------------------|-----------------------|
| n-hexadecane | 973 | 483 | 62 | 37.4 | 0 |
| Thiophene | 993 | 803 | 58 | 45.2 | 5 |
| (Me) ₂ S | 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: sulfur compound effects

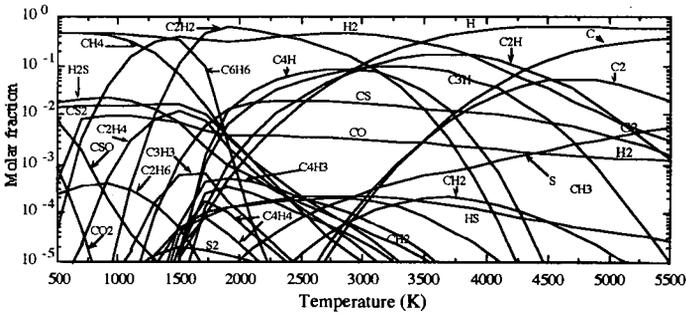


Figure 1: Complex Equilibrium of the system: C:H:O:S = 1 : 1.438 : 3.10⁻³ : 1.7.10⁻² at P=1atm.

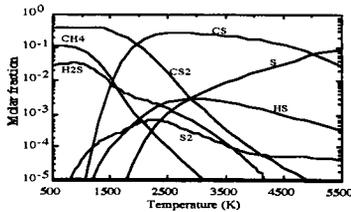


Figure 2: Complex equilibrium of the system: C:H:S = 4 : 4 : 1, at P=1atm

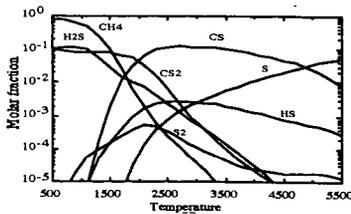


Figure 3: Complex equilibrium of the system: C:H:S = 4 : 12 : 1, at P=1atm

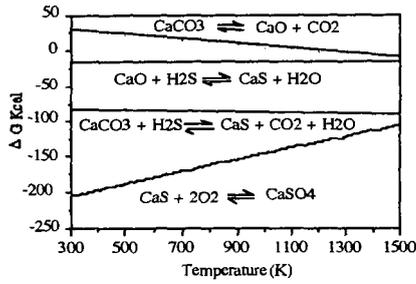


Figure 4: Free energy of different heterogeneous reactions versus temperature

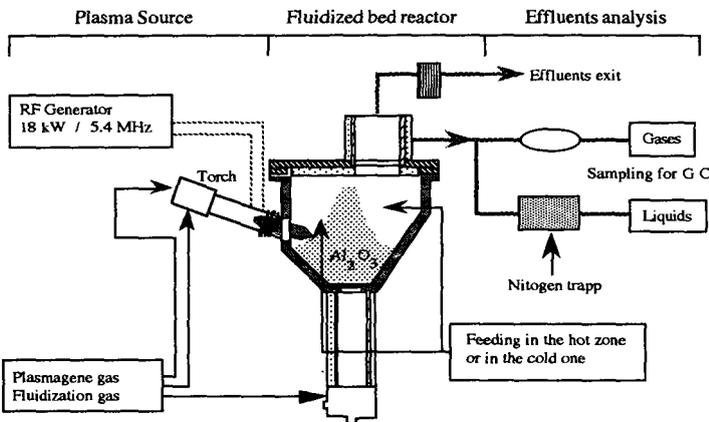


Figure 5: General flow sheet of the plasma fluidized bed reactor

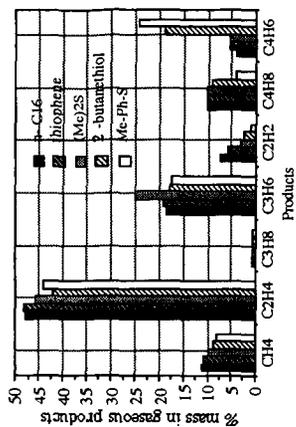
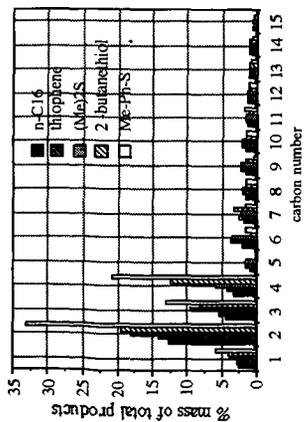


Figure 6: Products distribution for different mixtures with n-hexadecane (1% S)

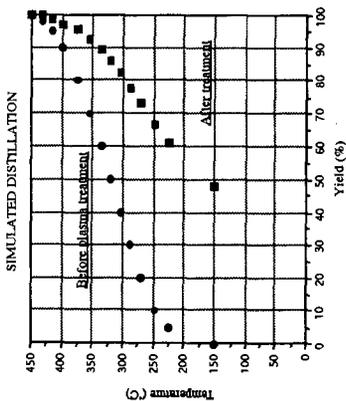


Figure 7: Results of gasoline hydroprocessing

Experimental parameters:

Pressure: 1 atm
 Plasma: A_{axial} = 15 l/min, Ar_{ig} = 12 l/min,
 H₂/g = 3 l/min, Fluidization: Ar = 39 l/min
 Power: 4.16 kW
 Particles: Al₂O₃: 450 g, ϕ = 350 μ m
 Feedstock: Gas oil (S=1.5 % wt), flow: 384 g/h
 Residence time: 0.3 sec, temperature: 740 °C