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CATALYTIC EFFECTS DURING THE THERMAL CRACKING OF HYDROCARBONS

EFECTOS CATALITICOS DURANTE LA REACCION TERMICA DE HIDROCARBUROS

Studies have been made of the pyrolysis of light hydrocarbons in the absence and presence of hydrogen at temperatures in the range 700-950 °C. Comparisons between the predictions of mathematical models and experiments have shown that the gas product yield spectrum can be explained by a reaction network based on homogeneous free-radical reactions without considering any surface interactions, and this has been confirmed by further experiments. Carbon formation, on the other hand, is influenced by the catalytic activity of the reactor wall.

1. INTRODUCTION

As a result of the increased importance of chemicals which can be obtained from light olefins, high temperature reactions such as steam cracking – which converts naphtha to ethylene, propylene and butenes – are attracting even more interest. The reactions are generally carried out at high temperatures, and are usually considered to be free-radical reactions occurring in the gas phase.

The conversion of naphtha to light olefins is essentially a pyrolytic reaction carried out in the presence of a diluent. The diluent may be steam (steam cracking) or may be hydrogen (hydrotreating): in the second case, the added gas also affects the chemistry of the overall reaction. Although it has long been known that the main reactions are free-radical, it has not been certain that only free-radical reactions are involved.

In recent years, attention has been focused on the mathematical modelling of these type of reaction, both as a means of verifying the consistency of a proposed mechanism and with the object of predicting the course of the overall reaction (1, 2). The problems with this approach are twofold. In dealing with rapid inter-related free-radical reactions, the complexity of the mathematical treatments presents many difficulties (3). In addition, experimental data used to test the models has been usually obtained by the use of batch or tubular flow reactors. Recent studies have shown that data obtained from a jet-stirred reactor is more reliable (4, 5), and gives results that are easier to model mathematically.

The present paper has two objectives. In the first, attempts have been made to model the free-radical reactions involved in the hydrotreating of ethane, in order to show – by comparison with experimental results obtained in a jet-stirred reactor – that the main reaction can be fully explained with a free-radical mechanism. Secondly, the possibility of catalytic effects of the reactor walls has been investigated experimentally.

2. EXPERIMENTAL

Experimental measurements were obtained using two jet-stirred reactors: these were designed to give good mixing at the required residence times (4). Product gas yields as a function of residence time were measured using a reactor of volume 6.63 cm^3 at room temperature. When the rate of carbon deposition was to be measured, a second, larger, reactor was used (volume 57.5 cm^3). This was designed in such a way that a metal liner could be inserted inside and a metal sample could be suspended from one arm of a C. I. Mark II microbalance near the nozzle of the jet.

Reactant gases (obtained in the highest possible purity from B.O.C.) were mixed at measured flow rates and taken to the reactor, which was maintained at a pre-set temperature. The products of reaction were passed through a glass wool filter to an on-line gas chromatographic analyzer, where the analysis was carried out to reproducibility (± 3 %).

The most complex experiments involved the measurements of gas yields and of carbon deposited. In these cases a circular piece of foil was suspended from the arm of the microbalance by a silica suspension, and a larger piece of metal was cut, bent and inserted in the reactor as a liner.

3. RESULTS

Data, intended for comparison with the mathematical model, was obtained using pure ethane or a mixture of ethane and hydrogen. The residence time, calculated in terms of the flow of inlet gas, was varied between 0 and 13 seconds, which covers the range of industrial interest (7). Typical product yields are presented graphically in figures 1, 2 and 3.

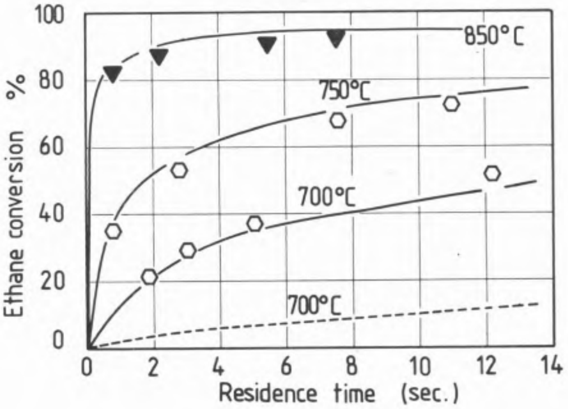


Fig. 1

Comparison of model prediction and experiments. Open symbols: pure initial ethane. Closed symbols: 54.8 % of ethane in hydrogen. Broken lines: model with initial parameters

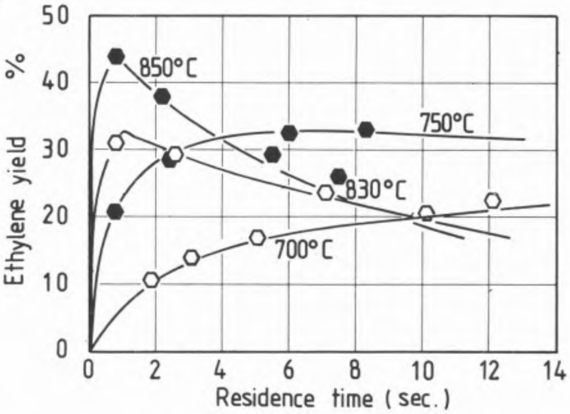


Fig. 2

Comparison of model predictions and experiments. Open symbols: pure initial ethane. Closed simbols: 54.8 % of ethane in hydrogen in feed. Lines: computer model prediction

Investigation of the inter-relation between gaseous products and carbon formation was carried out using propane as the main reactant. Gas product spectra using different materials lining the reactor walls are shown in figure 4: no significant differences were observed in the products compositions, indicating the lack of sensitivity of gas compositions with respect to the nature of the wall. Measurements of rates of carbon deposition was carried out in two ways. In the first, a fresh sample of the same metal was hung from the microbalance, and the weight uptake recorded as a function of time on line (figure 5).

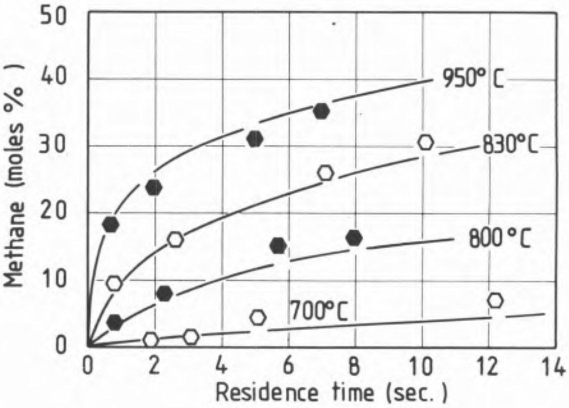


Fig. 3

Comparison of model predictions and experiments. Open symbols: pure initial ethane. Closed symbols: 54.8 % of ethane in hydrogen in the feed. Lines: computer predictions

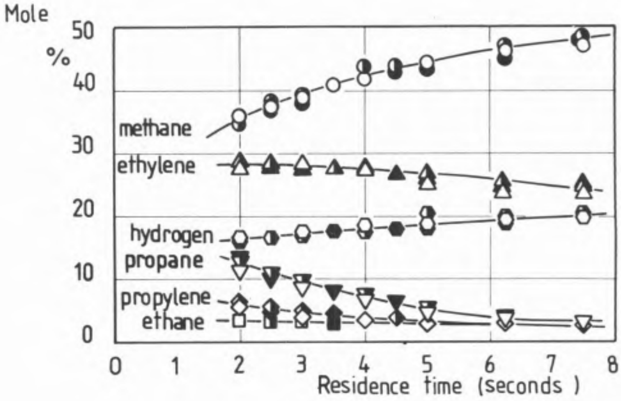


Fig. 4

Effect of different material liners on the product gas composition during the pyrolysis of propane. Open symbols: copper liner. Half closed symbols: nickel liner. Closed symbols: iron liner

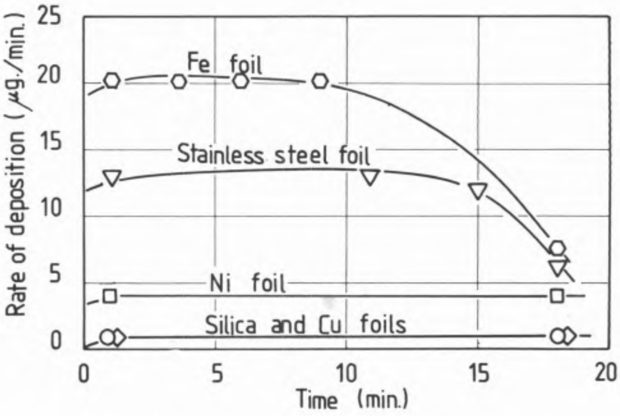


Fig. 5

Effect of the nature of the sample collection foil on the rate of carbon deposition. Pyrolysis of propane at 810 °C, 2 seconds residence time

4. DISCUSSION

4.1. MATHEMATICAL MODELLING OF GAS PRODUCT COMPOSITION

Inspection of the literature (1, 2, 3, 9, 10) allowed the generation of a plausible series of reactions, as shown in Scheme I; kinetic parameters, again obtained from the literature, are given in table 1. As a first step, the set of kinetic equations coupled together with the multicomponent mass balance of ideal continuous reactors, gave a model that was solved to predict product composition. Detailed account of the mathematical technique of solution of free radical models has been presented elsewhere (7).

SCHEME I

The free radical reaction model

$$C_2H_6 \xrightleftharpoons[k_{18}]{k_1} 2\ CH_3\cdot$$

$$C_3H_8 \xrightleftharpoons[k_{19}]{k_2} CH_3\cdot + C_2H_5\cdot$$

$$C_4H_{10} \xrightleftharpoons[k_{16}]{k_3} 2\ C_2H_5\cdot$$

$$C_2H_6 + H\cdot \xrightleftharpoons[k_{11}]{k_4} C_2H_5\cdot + H.$$

$$C_2H_6 + CH_3\cdot \xrightarrow{k_5} C_2H_5\cdot + CH_4$$

$$C_2H_5\cdot \xrightleftharpoons[k_8]{k_6} C_2H_4 + H\cdot$$

$$C_2H_5\cdot + C_2H_4 \xrightarrow{k_7} C_3H_6 + CH_3\cdot$$

$$H\cdot + C_3H_6 \xrightleftharpoons[k_{14}]{k_9} C_3H_7\cdot$$

$$H_2 + CH_3\cdot \xrightarrow{k_{10}} CH_4 + H\cdot$$

$$H_2 + C_3H_7\cdot \xrightarrow{k_{12}} C_3H_8 + H\cdot$$

$$C_2H_4 + CH_3\cdot \xrightleftharpoons[k_{15}]{k_{13}} C_3H_7\cdot$$

$$2\ C_2H_5\cdot \xrightarrow{k_{17}} C_2H_4 + C_2H_6$$

$$CH_3\cdot + H\cdot \xrightarrow{k_{20}} CH_4$$

$$C_2H_5\cdot + H\cdot \xrightarrow{k_{21}} C_2H_6$$

Table 1

Parameters of the model

Constant	Literature value	Source	After regression	Activation energy
i	log Ai		log Ai	Ei
1	16.79	(3)	16.63	86.0
2	18.2	(9)	18.26	85.0
3	17.9	(2)	17.9	86.3
4	12.58	(3)	15.28	7.0
5	11.40	(3)	8.92	10.8
6	14.72	(3)	15.87	40.8
7	9.6	(2)	11.52	19.0
8	13.73	(3)	15.91	5.4
9	10.79	(10)	10.79	4.5
10	11.28	(3)	11.28	9.5
11	12.25	(3)	10.43	11.4
12	9.0	(9)	9.0	8.0
13	8.0	(10)	8.0	7.0
14	14.41	(10)	14.41	39.5
15	11.70	(10)	11.70	25.0
16	13.78	(3)	13.96	0.0
17	13.0	(3)	13.0	0.0
18	13.84	(3)	13.84	0.0
19	13.84	(3)	14.13	0.0
20	8.0	(10)	8.0	0.0
21	12.0	(10)	12.0	0.0

As can be seen in figure 1 (broken line), this procedure gave some error between the predicted and measured gas conversions. As a result of this, attention was focused on upgrading the kinetic parameters, as these are known to the subject to error. A regression technique, based on the Gauss-Seidel method for algebraic models (8) was used to obtain upgraded values of the kinetic parameters (table 1). Solution of the model using these parameters gave more accurate predictions as shown in figure 1, 2 and 3 for pyrolysis and hydrogenolysis.

Inspection of literature and updated kinetic parameters summarised in table 2 shows that the new values are near to those previously reported. Also, the calculated standard deviation between the model

Table 2

Comparison of the parameters obtained with literature values

Constant	Log Ai (regression	Log Ai (literature)
1	16.63	16.29 (12), 16.70 (2)
2	18.26	18.2 (9)
4	15.27	14.32 (11)
5	8.91	12.2 (9), 8.5 (2)
6	15.87	14.0 (9), 14.72 (3)
7	11.52	9.6 (2), 12.8 (11)
8	15.91	14.1 (9), 13.8 (11)
11	10.43	11.7 (9)
16	13.96	12.88 (11), 13.78 (3)
19	14.13	13.4 (11), 13.85 (3)

predictions and the experimental results (4 %) is of the same order of magnitude as the experimental error (3 %). As a result, it can be seen that experimental results can be explained by a free-radicals homogeneous kinetic model.

Further proof that heterogeneous interactions do not play a significant role on the major gas reactions is given experimentally in figure 4, where composition differences amongst results obtained using different metal liners are well within the experimental error.

4.2. CARBON FORMATION

Inspection of the results summarised in figures 5 and 6 shows that this conclusion cannot be extended to the formation of carbon in the system. From figures 5 and 6 it can be seen that, in all cases the nature of the surface is affecting the rate of carbon formation, even when the surface that is being changed is physically separated from the surface on which carbon is being deposited (figure 6).

In that the chemical nature of the surface affects carbon formation, the shapes of the curves shown in figures 5 and 6 are not unexpected. At the start of a reaction, the metal surfaces will be carbon-free, and reactions leading to initial carbon will be dependent on the nature of the original surface. As the reactions proceed, the metal will become covered with carbon and the reactions leading to more carbon will be dependent on the new surface. The rate of production of more carbon should then be asymptotic to the same value – that for carbon deposition on a carbon surface. The observation that all surfaces were encapsulated with ordered carbon at the end of the experiment is entirely in agreement with this.

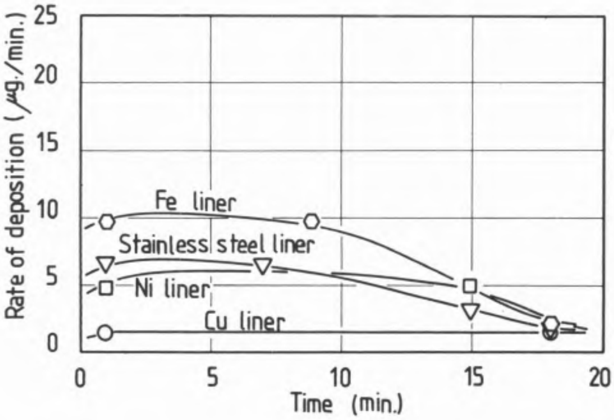
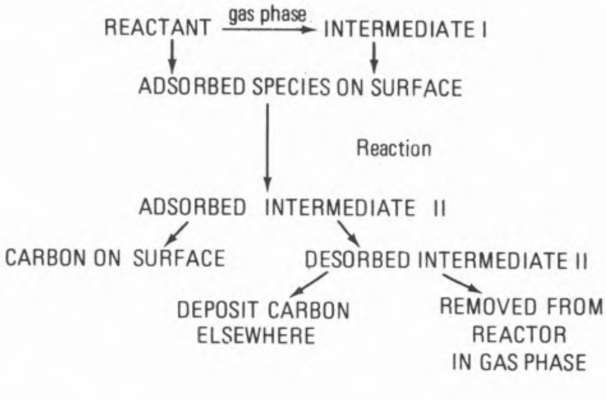


Fig. 6

Effect of reactor wall lining material on the rate of carbon deposition on a copper foil. Pyrolysis of propane at 810 °C, 2 seconds residence time

The fact that changes in the rate of carbon production do not accompany changes in the gas phase product spectrum is not unexpected. Calculation of yields show that the production of carbon is a minor reaction, and the effect of its formation on the overall mass balance is below the level of detection of gas chromatography.

Perhaps the most acceptable explanation of the fact that gas phase products are produced by a free-radicals gas phase reaction, while carbon production is influenced by the surface, lies in the suggestion that there are two concurrent processes occuring in the reactor, which may or may not interact. One of the processes is a free-radical reaction network as in Scheme 1 ; this is apparently independent of the surface. The other processes involves adsorption of a reactant or an intermediate on a surface, reaction to produce a carbon forming intermediate which may or may not desorb, followed by deposition of carbon elsewhere in the reactor.



The exact nature of these intermediates is open to question, although they are probably polynuclear aromatics. However, it is obvious that the extent of reaction on the surface, or even the nature of intermediate II, will depend on the chemical nature of the surface, as has been observed.

ACKNOWLEDGMENTS

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REFERENCES

1. HERRIOT, G. E., R. E. ECKERT and L. F. ALBRIGHT, A. I. Ch. E. Journal 18, 84 (1972).
2. PACEY, P. D. and PURNELL, J. H., I. E. C. Fundam. 11, 233 (1972).
3. SNOW, R. H., The Journal of Physical Chemistry 70, 2780 (1966).
4. BUSH, S. F., Trans. Inst. Chem. Engrs. 47, T59 (1966).
5. MULCAHY, M. F. R., «Gas Kinetics», Thomas Nelson & Sons, London, 1973.
6. THOMPSON, B. H. and T. C. BROOKS, «The production of methane by thermal hydrogenation of hydrocarbon oils». Presented to the 165 th A.C.S. National Meeting, Dallas, April, 1973.
7. LA CAVA, A. I., «Computer modelling and parameters estimation for ethane pyrolisis in the presence of hydrogen in a jet-stirred tank reactor». Thesis submitted for the M. Sc. Degree of the University of London, Imperial College, 1974.
8. SEINFELD, J. H., Industrial and Engineering Chemistry 62, 32 (1970).
9. KUNUGI T., T. SAKAI, K. SOMA and Y. SASAKI, Ind. Eng. Chem. Fundam. 9, 314 (1970).
10. BLACKEMORE, J. E. and CORCORAN W. H., Ind. Eng. Chem. Proc. Des. & Dev. 8, 206 (1969).
11. RATAJCZAK and TROTMAN-DICKENSON A. F., «Supplementary tables of bimolecular gas reactions», Cardiff, University of Wales Institute of Science and Technology, 1967.
12. LEATHARD D. A. and J. H. PURNELL, Ann. Rev. Phys. Chem. 21, 197 (1970).

RESUMEN

Se han realizado estudios de la pirólisis de hidrocarburos ligeros en presencia y ausencia de hidrógeno inicial a temperaturas en el rango de 700 a 950 °C. La comparación entre las predicciones de modelos matemáticos y los resultados experimentales han mostrado que el espectro de productos de reacción en la fase gaseosa puede ser explicado por un esquema complejo de reacción basado en reacciones homogéneas de radicales libres, sin considerar ninguna interacción con las superficies. Este hecho ha sido confirmado por posteriores experimentos. La formación de carbón, por otra parte, es afectada por la naturaleza y actividad catalítica de las paredes del reactor.

DISCUSSION

J. L. FIGUEIREDO : I would like to know if your results refer only to the high temperature region (higher than 700 ° C). You are reporting a rate of carbon formation on Fe higher than on Ni, and this is in fact the opposite to what happens at lower temperatures, where carbon deposition is catalytic (Cf. L. Lobo, D. L. Trimm, J. Figueiredo, Proc. 5th Int. Congr. Catal., Palm Beach, 1972).

A. LA CAVA : Yes, we worked at the high temperature region.