

KINETICS OF PYROLYSIS OF PETROLEUM RESIDUES.

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Introduction

The control of formation of mesophase is important for the quality of the products it may provide. Kinetic aspects are also relevant as they are related to the mechanism of mesophase formation. The objective of this work is to obtain a model of pitch pyrolysis and kinetic parameters.

Experimental

Material used.

Two petroleum residues (feedstocks) are used :

- an aromatic petroleum residue (R1).
- an aliphatic feedstock (R2)

Pyrolysis of the feedstocks.

Pyrolyses was carried out in a laboratory-sized pilot plant (1). In this study the temperature range of pyrolysis was 420-480 °C at pressures of 0.1 - 1.0 MPa.

Solvent extractions.

All the semicokes from pyrolyses were ground to < 500 µm particle size. 6 gram samples of semicoke were extracted with heptane at its boiling point, for two hours using a solid/solvent ratio of 1/20. The solvent of the soluble fraction was evaporated using a vacuum "Rotovapor". The fractions obtained were called HS and HI for the soluble and insoluble fractions respectively. The HI was then extracted with toluene at its boiling point, as with heptane. The soluble and insoluble fractions are called TS and TI respectively. The TI fraction was extracted with 1-methyl-2-pyrrolidinone at its boiling point, as with toluene. The soluble and insoluble fractions were called NMPS and NMPI, respectively. All the fractions were dried in a vacuum oven at 60 °C. Percentages of soluble and insoluble fractions (wt. %) are expressed in terms of the initial semicoke.

Optical microscopy.

All the samples were mounted in a resin block; optical polished surfaces were examined by reflected polarized light. The contents of isotropic (I) and anisotropic (A)

constituents were determined by the point-counting method.

Results and discussion

The process of formation of mesophase during pyrolyses was followed by formation of HI, TI, NMPI and A. Kinetic parameters for the production of insoluble material and anisotropy were obtained using the following assumptions:

- The insoluble products (HI, TI and NMPI) and anisotropy measured by optical microscopy (A) represent the mesophase content.
- The formation of mesophase follows apparent first order kinetics ($n=1$).

The equation applied is:

$$dX / dt = k (1-X)$$

in which X is represented by HI, TI, NMPI or A material. As an example, Figure 1 represents the plot of $\ln (1-HI/100)$ versus time for R1, 420-460 °C and 1.0 MPa.

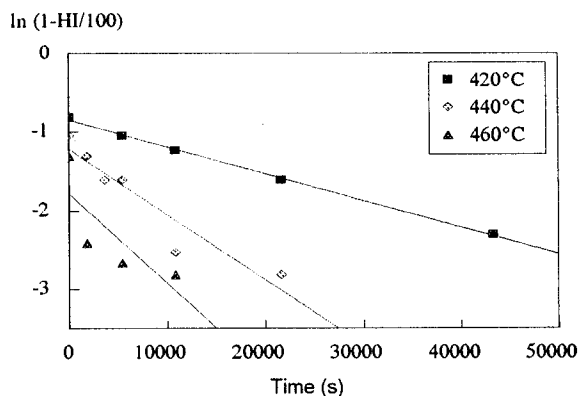


Figure 1. Plots of $\ln (1-HI/100)$ versus time of HI, R1 at 0.1 MPa

Values of activation energy (E_a) and pre-exponential factors (k_0) were calculated for the insoluble materials and A. (Table 1).

Table 1. Activation energies (Ea) and pre-exponential factors (Ko) for HI, TI, NMPI and A for R1 and R2

Feedstock	P (MPa)	X	Ea (kJ/mol)	Ko (s ⁻¹)
R1	0.1 MPa	HI	130	6 x 10 ⁴
R1	1.0 MPa	HI	200	1 x 10 ¹⁰
R1	0.1 MPa	TI	160	7 x 10 ⁷
R1	1.0 MPa	TI	230	1 x 10 ¹²
R1	0.1MPa	NMPI	160	9 x 10 ⁶
R1	1.0 MPa	NMPI	220	5 x 10 ¹¹
R1	0.1 MPa	A	190	4 x 10 ⁹
R1	1.0 MPa	A	240	1 x 10 ¹³
R2	0.1 MPa	HI	140	1 x 10 ⁶
R2	1.0 MPa	HI	180	3 x 10 ⁸
R2	0.1 MPa	TI	230	1 x 10 ¹⁵
R2	1.0 MPa	TI	240	2 x 10 ¹²
R2	0.1MPa	NMPI	200	1 x 10 ¹⁰
R2	1.0 MPa	NMPI	240	5 x 10 ¹²
R2	0.1 MPa	A	270	2 x 10 ¹⁵
R2	1.0 MPa	A	270	7 x 10 ¹⁴

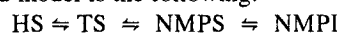
The experimental data and the obtained activation energies illustrate the following situations:

- Values of activation energy for anisotropy (A) are higher than those obtained by solubility.
- Activation energies increase in the order HI < TI ≈ NMPI < A.
- Plots of ln (1-X/100) (X=HI, TI and NMPI) versus time at maximum temperature or long pyrolysis time do not adjust well to first order kinetics, showing slower rates than predicted.
- The values of activation energies are pressure dependent, specially those from R1.
- R2 shows slightly higher activation energies than R1.

Some of these deviations can be explained with the following arguments:

- at the beginning of carbonization there is submicron mesophase which cannot be detected by optical microscopy which makes the rate constants a little lower at the beginning. At the end of carbonization there is soluble mesophase which makes the rate constants higher, at the end of carbonizations leading to higher activation energies when using anisotropy values.
- the measurements of different insolubles in measuring the kinetics of formation of different molecules, lead to different activation energies.
- the kinetics of formation is not a first order reaction. The shapes of the experimental curves for the change of solubility by increasing molecular weight are characteristic of consecutive reactions.

The proposed model is the following:



Theoretical values has been calculated from these equations by optimizing the values of activation energies and pre-exponential terms for the forward and reverse reactions. The theoretical curves adjust reasonably to the experimental data. Figure 2 is an example of these results for R2 at 440°C, 1.0 MPa

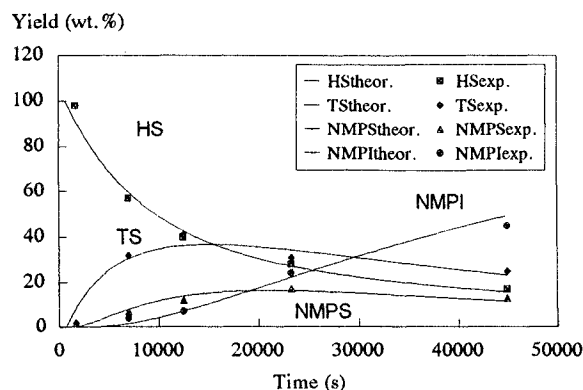


Figure 2. Experimental points and theoretical lines for the production of HS, TS, NMPS and NMPI at 440°C and 1.0 MPa.

This effect makes the reaction order different than 1 for the measurements of insoluble material. Also the possibility of reversibility can make the system go more slowly than predicted.

Conclusions

Kinetics of the pyrolysis of petroleum pitch have been obtained by using solvent extraction and optical microscopy. Values of activation energy are around 200 kJ/mol but varies depending upon the method used. The use of the fractionating solvent method suggests a consecutive model for the changes in solubility of the molecules formed during pyrolysis.

Acknowledgements

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