

KINETICS OF PITCHES NON-ISOTHERMAL HEAT TREATMENT

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Introduction

Pitch heat-treatments are involved in numerous industrial processes as activated carbon elaboration. As previously mentioned [1], pitch based activated carbon characteristics are drastically influenced by resins weight fractions. Moreover, during heat soaking, the three resins developments present antagonistic behaviours: the γ -resins disappearance and the α -resins formation lead to a first regime of β -resins formation followed by a second regime of β -resins consumption. Consequently, the yield of the first stage of pitch-based activated carbon elaboration process (prior to activation) has to be based on the optimization of the resins weight fractions as function of heat treatment temperature and duration. Nevertheless, few studies are available in the literature about model of pitch composition evolution during such heat soaking and they are usually restricted to the sole mesophase formation. A previous communication was focussed on pitch composition evolution under isothermal heat treatment [2].

Experimental

Experiments were performed in a stirred tank reactor already described in the isothermal part of the study [2]. The Ashland A240 petroleum pitch compositions were characterized after heat treatment by toluene and quinoline extractions in terms of α , β and γ resins weight fractions [2]. The heating rate was ranged from 0.5 to 5 K min⁻¹ and the final heat treatment temperature (FHTT) from 673 to 743 K.

Results and Discussion

As illustrated in Figures 1 to 3, the heating rate value R_H induced various effects on the resins weight fractions depending on the FHTT. At low FHTT, this effect on γ and β resins was linear and the corresponding slopes increased with FHTT. The α -resins weight fraction was not affected at low FHTT. At higher FHTT (723 K), non linear and strong effects of R_H were observed for the three resins corresponding to the α -resins formation regime. The extended model was based

on the basic mechanisms involved in the reactor (liquid-gas and liquid-liquid mass transfers, polymerization rate, liquid-liquid interfacial area growth and molecular weights evolutions [2]) and written by means of the mass balances of the three resins in term of moles:

$$\begin{aligned}dn_{\gamma}/dt &= -2 k_c(T) n_{\gamma}^2 V(t)^{-1} - k_g(T) a_{lg} n_{\gamma} \\dn_{\beta}/dt &= k_c(T) n_{\gamma}^2 V(t)^{-1} - k_{\beta l}(T) a_{l\alpha}(t) n_{\beta} \\dn_{\alpha}/dt &= k_{\beta l}(T) a_{l\alpha}(t) n_{\beta}\end{aligned}$$

where k_c was the kinetic constant of the polymerization reaction, k_g and $k_{\beta l}$ the gas-liquid and liquid-liquid mass transfer coefficients, a_{lg} and $a_{l\alpha}$ the liquid-gas and the liquid-liquid interfacial areas and V the liquid volume present in the reactor. The three kinetics parameters k_c , k_g and $k_{\beta l}$ were supposed to follow the Arrhenius behaviour through the corresponding activation energies.

The non-isothermal model was initiated by using the kinetics parameters identified under isothermal conditions. Therefore, the sole parameters identified under non-isothermal conditions were the involved-mechanisms activation energies. As shown in Figure 4, the experimental and optimized simulated data were in good agreement. Moreover, the optimized kinetics parameters obtained from isothermal and non-isothermal independent experimental data were found to be compatible.

In any case and considering a whole usual heat treatment, the heating rate chosen to reach the FHTT has an effect on the initial resins weight fractions of the plateau. Although few studies have been published on this area, processes based on pitches heat treatments need experimental data and mechanistic analysis under non-isothermal conditions for optimization.

Conclusions

The proposed whole mechanistic model is a useful tool for pitch composition optimization, reactor design and scale-up. It has been validated with success by confrontation to various experimental results and identified parameters (kinetics constants and activation energies) have been found to be in agreement with usual encountered values.

References

- [1] Daguerre E, Guillot A, Bonnamy S, Py X. Characterization of pitches used as activated-carbons precursors. Extended abstracts, Eurocarbon'98. Strasbourg (France), 1998;183-184.
- [2] Daguerre E, Py X, Guillot A. Kinetics of petroleum and coal-tar pitches evolution. Extended abstracts, Eurocarbon'98. Strasbourg (France), 1998;87-88.

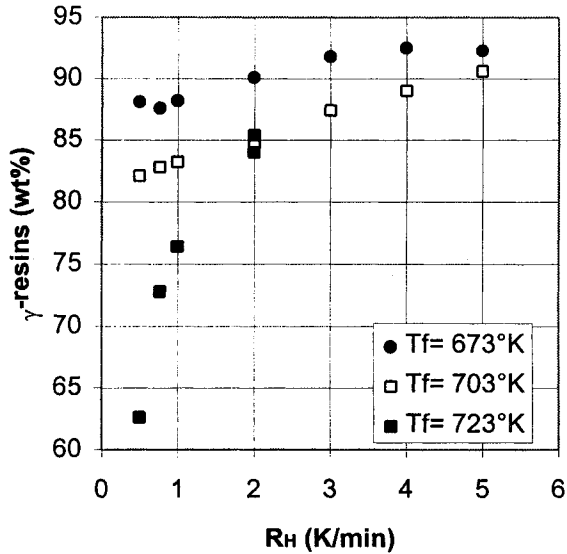


Figure 1. γ -resins weight fraction evolution with respect to R_H for three different FHTT.

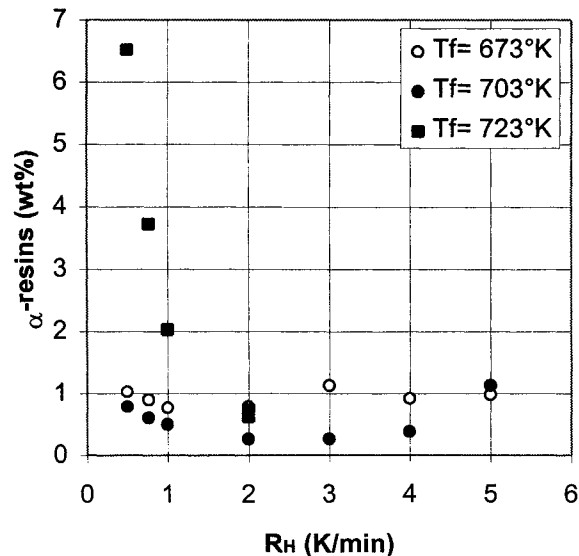


Figure 3. α -resins weight fraction evolution with respect to R_H for three different FHTT.

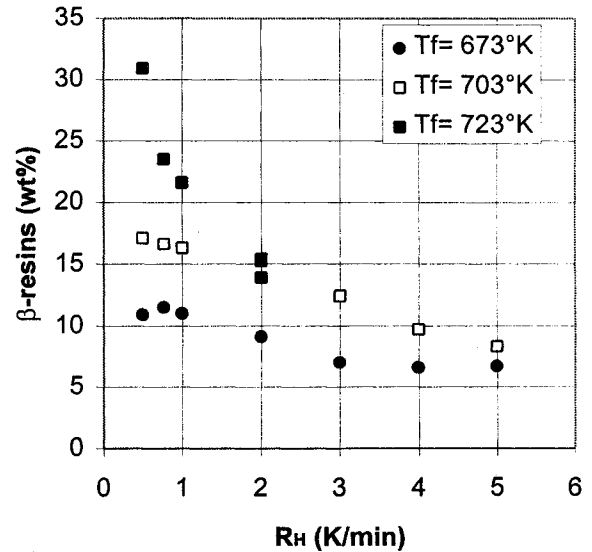


Figure 2. β -resins weight fraction evolution with respect to R_H for three different FHTT.

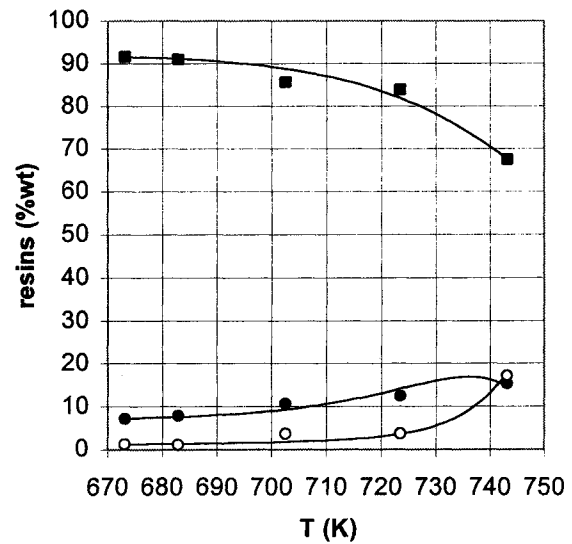


Figure 4. resins weight fractions evolution with respect to FHTT at $R_H = 2 \text{ K min}^{-1}$. (\blacksquare) γ -resins, (\bullet) β -resins, (\circ) α -resins, (-) model.

Acknowledgements

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