A KINETIC MODEL FOR CO-PROCESSING OF COAL AND WASTE TIRE

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ABSTRACT
Liquefaction of waste (recycled) tire and coal was studied both separately and using mixtures with different tire-to-coal ratios. Temperatures from 350-425°C were used. The data were analyzed using a model with a second-order consecutive reaction scheme (liquefaction to asphaltenes to oil and gas) for coal; a second-order conversion of tire to oil and gas; and an additional synergism reaction forming asphaltenes, first order in both coal and tire, when both are present. The agreement between the model and experiment was good.

INTRODUCTION

Disposal of used tires is a major environmental problem. Liquefaction of such tires in conjunction with coal has been suggested as an alternative to their disposal [1-3]. Farcasiu and Smith [1] studied the co-liquefaction of tire and Illinois #6 coal at 425°C and observed a synergistic effect of tire on coal conversion. Similar results were obtained at 400°C by Liu et al. [2] for the liquefaction of DECS-6 coal with a tire sample prepared from an used Goodyear Invicta tire. In all these studies a complete conversion of the volatile matter of the tire was obtained.

In this work, co-liquefaction of DECS-6 coal and a waste tire sample was studied at 350-425°C. Runs were made with tire and coal separately as well as by using mixtures with tire/coal ratios of 0-4. The hydrogen pressure was kept at 1000 psi (cold). The data were analyzed using a second-order consecutive reaction scheme for the liquefaction of coal to asphaltenes and then to oil and gas.

EXPERIMENTAL

The coal used was DECS-6 which is a high-volatile-A bituminous coal from the Blind Canyon seam in Utah. The tire sample was obtained from the University of Utah Tire Bank and represented mixed recycled tires ground to -30 mesh. The proximate and ultimate analyses showed that the coal contained 49% volatile matter (on a dry, ash-free basis) and 51 wt% fixed carbon. The amounts of volatile matter and fixed carbon in tire were 71 wt% and 29 wt%, respectively. The fixed carbon essentially represents the content of carbon black in the tire.

The details of the experimental equipment, run procedures and analytical techniques have been described earlier [4]. A stainless-steel tubing bomb reactor with a volume of 27 ml was used for the liquefaction. The reactor was loaded with the feed, purged and pressurized with H_2 to 1000 psi (cold). The feed consisted of tire or coal or a mixture of the two in different ratios. The gaseous products were collected and analyzed by gas chromatography. The solid and liquid products in the reactor were washed and extracted with tetrahydrofuran (THF) for 24h. The THF-insoluble material (TI) was separated by filtration. The conversion is calculated from the amount of THF-insoluble material. After the removal of THF by rotary evaporation, the THF-solubles were extracted with hexane for 2h. The extract was separated into hexane-insoluble (HI) and hexane-soluble (HS) fractions by filtration. The THF-soluble/ hexane-insoluble fraction, i.e. the HI fraction, represents asphaltenes. The HS fraction was the 'oil'. The oil yield was obtained by difference. In many cases, the combined oil + gas yield was calculated by difference. Most runs were made in duplicate and the experimental error was ±2.5%.

In the co-liquefaction runs, the overall conversion and the yields of asphaltenes and oil + gas fractions were calculated as above. However, in order to get a better insight, the results were also analyzed in terms of incremental conversion and yields, based on coal, which were calculated as follows;

$$X_{cm} = (X_{ov} - w_t X_t)/w_c \qquad (1)$$

where X_{ov} is the total conversion and w_t and w_c are the weight fractions of tire and coal in the feed, respectively. In equation (1), X_{cm} is the conversion of the mixture on a coal-alone basis and X_t is the conversion of tire alone under the same conditions. The yield of asphaltenes on a coal-alone basis was calculated similarly. The oil+gas yield from coal was calculated by difference.

RESULTS AND DISCUSSION

Effect of R_{TC} and Temperature

Figure 1 shows the effect of tire-to-coal ratio (R_{TC}) on conversion and oil+gas yield at 375°C. The results are presented on a coal-alone basis, i.e., the contribution of the tire has been subtracted. The conversion increases from 30% (at R_{TC}=0) to about 40% at R_{TC}=4. This indicates that the addition of tire has a synergistic effect on coal conversion. The synergistic effect is mainly towards the asphaltenes since the oil+gas yield is essentially unaffected by the addition of the tire.

The results at 400°C, presented in Figure 2, indicate a significant effect of R_{TC} on conversion, especially at low values of R_{TC}. The conversion of coal alone increases from 35% (without tire) to 49% when R_{TC}=1. At higher R_{TC} values, the addition of tire has only a small effect on coal conversion. There seems to be slight maximum in the conversion at R_{TC}~3, where the conversion is 54%. The decrease in conversion at high R_{TC} may be due to a low concentration of coal in the reaction mixture. The oil+gas yield decreases more-or-less linearly with increase in R_{TC}.

Similar observation are made from the results obtained at 425°C (Figure 3). In this case, the maximum conversion is over 70% at R_{TC}=1. The oil+gas yields at 425°C are also higher than those at 400°C.

Data Analysis

Since oil and gas are the major products of tire liquefaction, the liquefaction of tire (TR) is essentially represented by:

$$TR \xrightarrow{k_{tr}} OG \qquad (2)$$

For coal liquefaction, the experimental data suggest a predominantly consecutive reaction scheme with liquefaction of coal (C) to asphaltenes (A) and oil+gas (OG).

$$C \xrightarrow{k_t} A \xrightarrow{k_a} OG \qquad (3)$$

In the presence of the tire (TR), the conversions increase due to the synergism by the free-radical reactions between coal and tire. The synergism is mainly towards asphaltenes and is represented by:

$$C + TR \xrightarrow{k_s} A \qquad (4)$$

Now, the rates of conversion of tire (r_{tr}) and coal (r_c), and the rate of asphaltenes formation (r_a) are:

$$r_{tr} = k_{tr}C_{tr}^2 + k_sC_{tr}C_c \qquad (5)$$

$$r_c = k_tC_c^2 + k_sC_{tr}C_c \qquad (6)$$

$$r_a = k_tC_c^2 + k_sC_{tr}C_c - k_aC_a^2 \qquad (7)$$

where C_{tr}, C_c and C_a are the mass fractions of tire, coal and asphaltenes, respectively. In order to minimize the correlation between the activation energy and the pre-exponential factor, the rate constants were reparametrized to the form:

$$k = k(M)\ \exp[E\{1/T(M)-1/T\}/R] \qquad (8)$$

with k and k(M) being the values of the rate constant at T and T(M); E and R represent the activation energy and universal gas constant. The results are presented in Table 1. The rate constant for the liquefaction of tire (k_{tr}) is higher than that for the coal (k_t), as expected. The activation energies for both the liquefaction of coal and tire are low indicating a possible pore diffusion effect. The activation energy (E_a) for k_a was found to be not significantly different from zero indicating that the rate of asphaltene-to-oil+gas reaction is not dependent on temperature.

The experimental values of the overall conversion (of coal+tire) and overall yield (of oil+gas) are compared in Figure 4 with values calculated from the parameters of Table 1. The comparison seems satisfactory, considering the complexity of coal/tire co-liquefaction.
The model shows that the synergistic effect of tire is strongly dependent on the process conditions. Both the observed and predicted conversions decrease above 400°C when R_{TC} is 2. The oil+gas yields are governed mainly by the concentration of asphaltenes, increasing with an increase in asphaltene concentration.

CONCLUSIONS

1. The conversion and product yields from coal and tire are strongly dependent on temperature.
2. The co-liquefaction of tire with coal has a considerable synergistic effect on the conversion and asphaltene yield from coal. The synergism increases with an increase in tire/coal ratio, at least up to a tire/coal ratio of 1.
3. A consecutive reaction scheme for the conversion of coal to asphaltenes and oil+gas represents the data reasonably well at various temperatures and tire/coal ratios. The model uses second-order kinetics for the separate liquefaction of coal and tire and an overall second-order rate expression for the co-liquefaction (synergism reaction).

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Table 1. Summary of Kinetic Results[a]

Rate Constant	k(M)* [Min^{-1}]	Activation Energy [kJ.mole^{-1}]
k_{tr}	4.0±1.1	24.4±6.9
k_t	1.0±0.4	35.7±7.2
k_a	6.8±1.8	0
k_s	3.6±0.6	83.8±27.4

[a]±represents 95% confidence limits; *k at 673K.

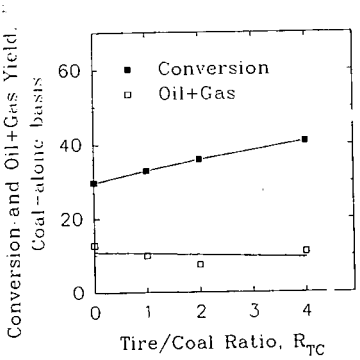

Figure 1. Effect of R_{TC} on co-processing of coal and waste tire at 375°C. Other conditions: 30 min, 1000 psi H_2 (cold).

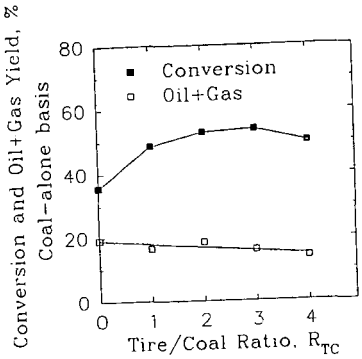

Figure 2. Effect of R_{TC} on co-processing of coal and waste tire at 400°C. Other conditions same as in Figure 1.

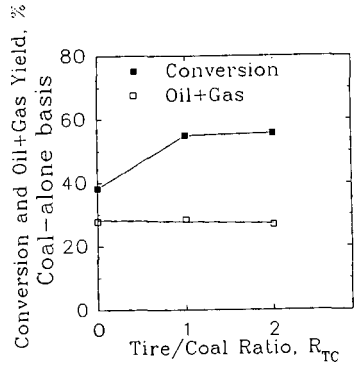

Figure 3. Effect of R_{TC} on co-processing of coal and waste tire at 425°C. Other conditions same as in Figure 1.

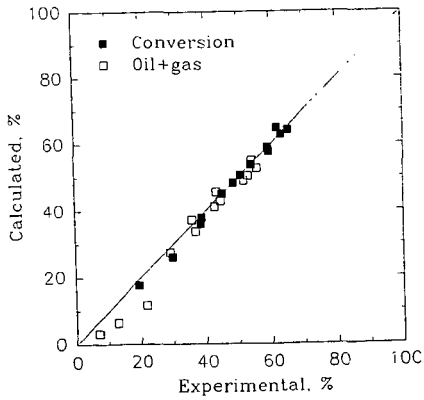

Figure 4. Comparison of the experimental and calculated values of the conversions and oil+gas yields from coal/tire co-processing