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Catalysis Today 40 (1998) 307–320

CATALYSIS TODAY

Effect of process conditions on co-liquefaction kinetics of waste tire and coal

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Abstract

Thermal and catalytic liquefactions of waste (recycled) tire and coal were studied both separately and using mixtures with different tire/coal ratios. Runs were made in a batch tubing bomb reactor at 350–425°C. The effect of hydrogen pressure on the product slate was also studied. Mixtures of tire components and coal were used in order to understand the role of the tire as a solvent in co-liquefaction. In the catalytic runs, a ferric-sulfide-based catalyst impregnated in situ in the coal was used. Both the tire components and the entire tire exhibit a synergistic effect on coal conversion. The extent of synergism depends on temperature, H_2 pressure and the tire/coal ratio. Experiments with coal and tire components show that the synergistic effect of tire is due to the rubber portion of the tire and not the carbon black. The synergism mainly leads to an increase in the yields of asphaltenes, which are nearly double those in the coal-only runs at 400°C. The conversion of coal increases dramatically using the catalyst, but the catalytic effect is attenuated somewhat in the presence of tire, especially at high tire/coal ratios. The data were analyzed using a consecutive reaction scheme for the liquefaction of coal to asphaltenes and thence to oil+gas, both reactions being of second order; a second-order conversion of tire to oil+gas; and an additional synergism reaction when both coal and tire are present, first-order in both coal and tire. Parallel schemes were assumed for thermal (uncatalyzed) and catalyzed reactions. The uncatalyzed liquefaction of coal has a low apparent activation energy, 36 kJ/mol, compared to those for the synergism reaction (84 kJ/mol) and the catalytic coal liquefaction (158 kJ/mol). The conversion of asphaltenes to oil+gas is relatively independent of temperature and of the presence of the catalyst. The catalyst appears to play a significant role in the conversion of coal to asphaltenes, but a negligible role in the synergism reaction.

Keywords: Kinetics; Catalytic; Co-liquefaction; Coal; Tire

1. Introduction

The disposal of waste tires is a major environmental problem. Recently, the liquefaction of such tires in conjunction with coal was suggested as an alternative for their disposal [1,2]. Farcasiu and Smith [1] used Illinois No. 6 coal and observed a synergism due to tire at 425°C. Liu et al. [2] studied the co-liquefaction of a tire and coal from the Blind Canyon seam in the absence of an additional solvent, and observed a synergistic effect of the tire on coal conversion. The conversion of coal was shown [3] to increase further when a ferric-sulfide-based catalyst was used in the co-liquefaction. The tire in these studies [2,3] was prepared "in-house" from a used Goodyear Invicta tire and the liquefaction was performed at 400°C. In another study [4], it was observed that, even at the

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PII S0920-5861(98)00060-1

most mild conditions (350°C, 15 min), over 70% of the organic material in the tire was converted into products in the oil range.

Table 1 shows the composition of a typical tire. The tire contains about 35 wt% styrene-butadiene rubber (SBR), 8 wt% polybutadiene rubber (PBR), 20 wt% aromatic oil and 33 wt% carbon black, in addition to small quantities of zinc oxide, sulfur, and other, unspecified, miscellaneous components [1]. It is not clear from the literature which of these components could contribute to the synergism in co-liquefaction. Some of the tire components probably depolymerize during liquefaction to produce free radicals that are relatively stable [5]. Coal liquefaction too is known to produce free radicals, and the recombination reactions among these radicals are considered to be the major retrogressive reactions for coal liquefaction at high temperatures [6]. Accordingly, it has been suggested [2] that the stabilization of the free radicals of the coal by the free radicals in the tire minimizes the retrogressive reactions and increases the conversion of coal. Further, the liquid product formed from the tire could improve the hydrogen shuttling properties of the reacting system. Hence it would appear that the tire material may be acting in a similar manner to a process solvent during coal liquefaction. However, as argued by McMillen et al. [7], the relative rates and efficiencies of radical stabilizing steps are determined by process conditions. This indicates that the extent of synergism, and therefore the efficiency of co-liquefaction, may vary with the conditions of the process, i.e., the temperature, pressure, time and coal-to-tire ratio.

As mentioned above, in our earlier work, the tire sample was prepared "in-house" and the liquefaction was performed at a single temperature [3]. It is of interest to study the coal/tire co-liquefaction under varying conditions of temperature, H_2 pressure and tire/coal ratio using a "standard" sample from mixed recycled waste tires and a ferric-sulfide-based catalyst impregnated in the coal. This catalyst has been shown to be a superior iron-based catalyst for direct coal liquefaction [8]. The effects of process conditions on the activity of the ferric-sulfide-based catalyst for the co-liquefaction also need to be investigated further.

In this work, the tire sample was obtained from the University of Utah Tire Bank and represents mixed recycled automobile waste tires. The effects of temperature, H_2 pressure and tire/coal ratio on the co-liquefaction of tire and coal were studied systematically in detail. Runs were made with tire components, recycled tire mixture, and coal separately, as well as with binary mixtures including coal, in order to assess the role of tire as solvent. The temperature was in the range 350–425°C and the hydrogen pressure was varied between 0 and 1500 psi (cold). In the catalytic runs, the ferric-sulfide-based catalyst was impregnated in situ in the coal under various conditions, in order to study the effect of catalyst preparation on co-liquefaction.

2. Experimental

2.1. Materials

The coal used was DECS-6, a high-volatile-A bituminous coal from the Blind Canyon seam in Utah. The coal was received from the Pennsylvania State University Coal Bank (PSUCB) and was ground to −60 mesh under nitrogen. The analysis provided by PSUCB indicates that the coal has a low iron content (0.3%). The individual components of the tire, as listed in Table 1 (but excepting the "miscellaneous" components) were provided by Dr. M. Farcasiu of the Pittsburgh Energy Technology Center of USDOE. The carbon black was Mogul 1 from Cabot Corporation. Zinc oxide and sulfur were obtained from Aldrich and Fisher Scientific, respectively. All other components were from Michelin America Small Tire [1]. The sample of the whole tire ("Tire-2") was obtained from the University of Utah Tire Bank and represents mixed recycled automobile tires, with nylon cords and steel belts removed, ground to −30 mesh.

Table 1
Composition of tire rubber [1]

Component	wt%
Styrene-butadiene rubber (SBR)	35
cis-Polybutadiene rubber (PBR)	8.5
Aromatic oil (from petroleum)	20
Zinc oxide	1
Sulfur	1
Carbon black	33
Miscellaneous (accelerators, etc.)	1.5
Total	100.0

Table 2
Proximate and ultimate analyses of coal and tire[a]

Sample	H_2O (%)	Ash (% dry)	Volatile matter (% daf)	Fixed carbon (% daf)	C (%)	H (%)	N (%)	S (%)	O[b] (%)
DECS-6	1.8	6.3	49	51	81.9	6.3	1.5	0.9	9.4
TIRE-2[c]	0.4	8.1	71	29	79.6	7.4	<0.5	1.7	11.2
TIRE-1[d]	0.3	4.7	67	33	84.3	7.4	<0.5	1.6	6.7

[a] From Galbraith.
[b] Obtained by difference.
[c] Used in this study.
[d] Used by Liu et al. [2,3].

Proximate and ultimate analyses of the coal and tire samples used in the present work were performed at Galbraith. The results are presented in Table 2. The analyses show that the fixed carbon in the tires is essentially carbon black. For the sake of completeness, also shown in Table 2 (as "Tire-1") is the analysis of the "in-house" tire sample used previously [2]. The two tires are remarkably similar, except that the ash content and the O-content of Tire-2 are somewhat larger than the corresponding values of Tire-1. The ash probably consists of inorganic components such as zinc, sulfur, titania and other additives used as binders in the tire. Also, it should be noted that the oxygen content in the ultimate analyses is obtained by difference, i.e., this entry contains everything that is not C, H, N, or S. Since the Tire-1 sample is from a single tire, while Tire-2 consists of a composite of many tires, the latter is probably closer to the average composition expected in a commercial unit.

In the catalytic runs, the ferric-sulfide-based catalyst was impregnated in situ in the coal according to the method described by Liu et al. [3]. In brief, solutions of a ferric salt and a sulfide were added in succession to the coal, which was then filtered, washed and dried. The catalyst loading was kept constant at 1.67% by weight, based on dry ash-free (daf) coal, which corresponds to an iron loading of approximately 0.9%. The impregnated coal was dried under vacuum at different temperatures, ranging from 25°C to 150°C, to determine the effect of drying temperature on catalyst activity. The catalyst prepared thus has been shown [3] to have a surface area of 84 m^2/g and an average particle size of 18 nm.

2.2. *Run procedure*

A stainless-steel tubing-bomb reactor with a volume of 27 ml was used for the liquefaction. The reactor was loaded with the feed, and purged and pressurized with H_2 and/or helium to the desired pressure. The feed consisted of tire or coal or a mixture of the two in different proportions. In every case, the total mass of feed was kept constant at 3 g. The liquefaction runs were carried out at 350–425°C. The reactor was placed in a fluidized sand bath which was preheated to the desired temperature before the run. During the run, the reactor was continuously shaken vertically at 500 cycles/min using a crank mechanism. At the end of the run, the reactor was quenched in water.

The gaseous products were collected in an evacuated flask of known volume (nominally 1000 ml) and analyzed by gas chromatography. For this purpose, an aliquot (2 ml) of the gas was injected into a gas chromatograph (Shimadzu GC-8A) which was equipped with a thermal conductivity detector. A 6 m×3 mm nickel column containing a 100/200 mesh Hayesep-D packing (from Alltech) was used. Hydrogen was used as the carrier gas, so that the hydrogen signal from the product gas would not swamp those from the other components. The oven was programmed to operate from 30°C to 200°C at 20°C/min. The peak identification was done using calibration gases. Among the gases present, ethane was a median and major component. Since the amount of gas product was small (5 wt%), the total amount of gas was calculated, for convenience, on an ethane-equivalent basis, i.e., assuming that the calibration factors for all the components were the same as that for ethane. In this way, the amount of gas, as well as its composition, were obtained on a hydrogen-free basis. A component-by-component analysis of the gas under different process conditions has been presented earlier [2].

The solid and liquid products in the reactor were washed and extracted with tetrahydrofuran (THF) for 24 h. The THF-insoluble material (TI) was separated by filtration. The amount of TI material is used to calculate the conversion, as shown below. After the removal of THF by rotary evaporation, the THF-solubles were extracted with hexane for 2 h. The resulting mixture 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 percent conversion (X) and the yield of asphaltenes (A) were calculated as follows:

$$X = (F_{\mathrm{d}} - \mathrm{TI})/F_{\mathrm{daf}} \times 100, \tag{1}$$

$$A = \mathrm{HI}/F_{\mathrm{daf}} \times 100. \tag{2}$$

Here F_{d} and F_{daf} represent the amount of feed on a dry basis and a dry, ash-free (daf) basis, respectively. The gas yield (G) was determined independently from the gas analysis. The oil yield (O) was obtained by difference:

$$O = X - A - G. \tag{3a}$$

In general, the gas yields are small and relatively constant. Hence, in many cases, the gas yield was not separately determined, and the combined oil+gas yield (OG) was calculated by difference:

$$OG = X - A. \tag{3b}$$

In the co-liquefaction runs, the overall conversion and the overall yields of asphaltenes and oil+gas fractions were calculated as above. However, the results were also analyzed in terms of conversion and yields based on coal alone. This allows us to compare co-liquefaction results with those of coal liquefaction. The conversion on a coal-alone basis, X_{CM}, was estimated as follows:

$$X_{\mathrm{CM}} = (X_{\mathrm{OV}} - W_{\mathrm{TR}}X_{\mathrm{TR}})/W_{\mathrm{C}}. \tag{4}$$

Here X_{OV} is the overall conversion and X_{TR} is the conversion of the tire alone under the same conditions. W_{TR} and W_{C} are the weight fractions of tire and coal in the feed, respectively, such that

$$W_{\mathrm{TR}} + W_{\mathrm{C}} = 1.$$

The yield of asphaltenes on a coal-alone basis and the gas yield on a coal-alone basis were calculated similarly. The oil+gas yield on a coal-alone basis (or the oil yield on a coal-alone basis) was calculated by difference.

For co-liquefaction runs, it is difficult, if not impossible, to assign products unambiguously to either the coal or the tire component, and we have not attempted to do so. Assuming that such an assignment were possible, it is reasonable to expect that the conversion and yields from the tire in co-liquefaction runs would be different from those in tire-alone runs. It should be recognized that the steps used in calculating the conversions and yields on a coal-alone basis (Eq. (4)) do not assume that the conversion and yields from the tire are the same as that from the tire component of the co-liquefaction runs. Rather, the calculation approach simply "lumps" the entire incremental effect of co-liquefaction into a single component, viz., coal. Such a calculation procedure allows the results of runs with coal and tire and runs with coal alone to be compared on a systematic basis.

All runs were made in duplicate. The experimental error (on an absolute basis) is ±2 percentage points for each of the conversions and asphaltene yields, and ±4 percentage points for the oil+gas yields. The gas yields varied by less than 1 percentage point.

3. Results and discussion

3.1. Separate liquefaction of tire components

The tire components listed in Table 1, with the exception of "miscellaneous", were combined in the proportions of Table 1 and were liquefied at 400°C for 30 min under a H_2 pressure of 1000 psi (cold). It was found that nearly 96 wt% of the amount of non-carbon-black components was converted (on a carbon-black-free basis), i.e., essentially all the organic components were converted to oil+gas product. When the experiment was repeated in the absence of the carbon-black component, the conver-

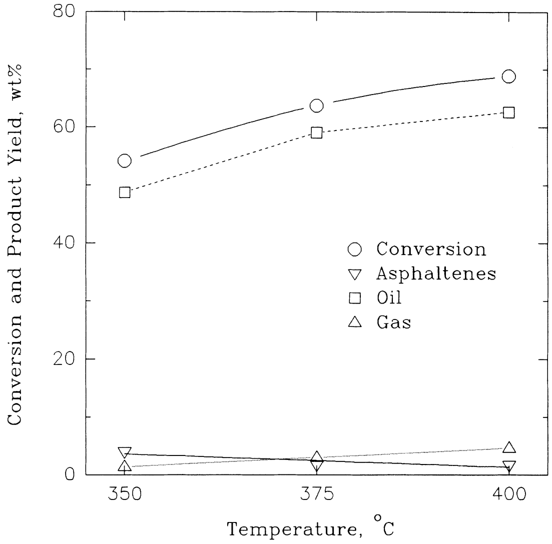

Fig. 1. Effect of temperature on liquefaction of recycled tire. Reaction conditions are: 1000 psi H_2 (cold), 30 min.

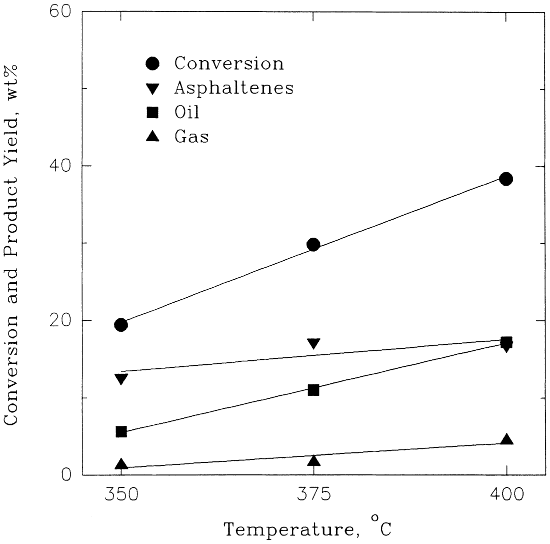

Fig. 2. Effect of temperature on liquefaction of coal. Reaction conditions are the same as in Fig. 1.

sion was not affected by the addition of carbon black to the mixture. The amount of asphaltenic product was negligible in each case.

3.2. *Separate liquefaction of entire tire and coal*

3.2.1. *Effect of temperature*

The results from tire liquefaction are presented in Fig. 1. At 400°C, the conversion of tire is about 69 wt% which corresponds to almost the entire organic portion of the tire. The product is mostly oil, with a small amount (4.5 wt%) of gaseous product, and with asphaltene yield virtually indistinguishable from zero. Therefore, almost all the organic portion of the tire is converted to oil+gas product, as observed above with the tire components, and previously by Farcasiu and Smith [1] and Liu et al. [2]. The conversion decreases with decreasing temperature. The yield of oil also decreases. The amounts of both asphaltenes and gaseous product are small at all the temperatures. Fig. 1 indicates that the selectivities to various products (i.e., the ratios of product yield to conversion) are independent of temperature. This suggests that the nature of the polymeric bonds which undergo cracking during the liquefaction of the tire is not altered by the temperature.

The results from coal liquefaction at different temperatures are presented in Fig. 2. The conversion and the product yields depend on temperature. For the conversion and the oil yield, in particular, the effect of temperature is more pronounced for the case of the coal than for the tire. The relatively low values observed for the conversions are due to the absence of a solvent, hydrogen donor, and catalyst. Asphaltenes are a major product at all the temperatures of Fig. 2, and are more-or-less constant at 17 wt%. This is in contrast to the results from tire liquefaction, where the yield of asphaltenes is negligible.

The nature of the products from coal is different from those corresponding to the tire, as is to be expected. The above results suggest that coal radicals have a wide size distribution, covering the range of both the oil and the asphaltene fractions, whereas the radicals from tire have a relatively narrow distribution, which is mainly in the oil range. The decrease in the yield of asphaltenes at high conversions and the low yield of oil+gas at 350°C suggest a predominantly consecutive reaction scheme for the liquefaction of coal to asphaltenes and oil+gas, i.e., the direct liquefaction of coal to oil+gas is relatively small. In an earlier study [4], we varied the reaction time between 15–60 min and observed essentially the same product

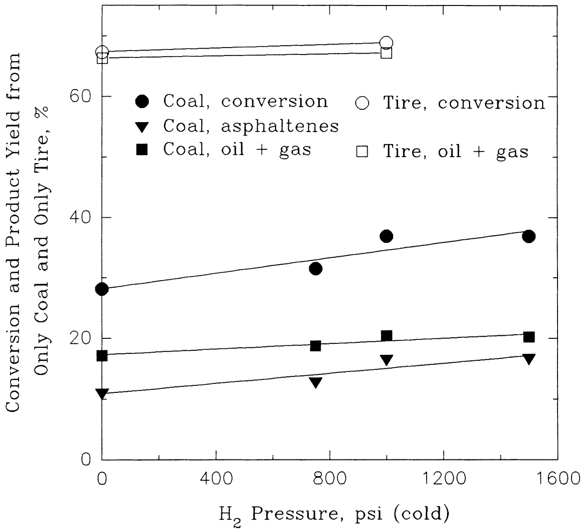

Fig. 3. Effect of H_2 pressure on liquefaction of coal and tire separately. Reaction conditions are: 400°C, 30 min.

distribution, indicating that the reaction scheme does not vary significantly with reaction time under the conditions used in this study.

3.2.2. *Effect of* H_2 *pressure*

Fig. 3 shows the effect of hydrogen pressure on the separate liquefactions of tire and coal at 400°C. It should be noted that the combined oil+gas yield is shown in this figure; in Figs. 1 and 2, the oil yield and the gas yield are shown separately.

The conversion and oil+gas yields from tire are not affected by the hydrogen pressure. This suggests that the radicals from the tire do not require any stabilizing agent.

In the case of coal, the conversion increases from 28%, in the absence of hydrogen, to 37% at a hydrogen pressure of 1000 psi (cold) or above. Correspondingly, the yields of both asphaltenes and oil+gas fractions increase. Therefore, it seems that the gaseous hydrogen helps to stabilize the coal radicals to prevent their recombination by retrogressive reactions. The results are consistent with the observations of Malhotra and McMillen [6] and Whitehurst et al. [9], that the retrogressive reactions in coal liquefaction become more pronounced under hydrogen-deficient conditions. However, under the conditions used in Fig. 3, i.e., in the absence of a solvent or catalyst, only a limited amount of hydrogen may be used.

3.3. *Co-liquefaction of tire components and coal*

In order to understand the effect of various tire components on the liquefaction of coal, two mixtures were prepared for co-liquefaction with coal. The first mixture contained all the tire components of Table 1 except "miscellaneous" and carbon black, and the concentration of each component was as in Table 1. The second mixture consisted of all the components except "miscellaneous", this time including carbon black, in the proportions given in Table 1. These mixtures were co-liquefied with coal at 400°C and 1000 psi H_2 pressure (cold) using equal parts by weight of the tire-component mixture and coal. The conversion on a coal-alone basis, X_{CM}, was 57 wt% when coal was liquefied with the first mixture. The yield of oil+gas was 21 wt%. Using the second mixture, i.e., with carbon black, an essentially similar conversion and oil+gas yield were obtained. The above conversion values are about 20% points higher than those in the coal-alone runs. However, the oil+gas yields in these co-liquefaction runs are similar to those in the coal-alone runs.

Note that the effect of the tire components acting alone has been subtracted from the overall co-liquefaction results to obtain the results on a coal-alone basis. Therefore, the difference between the co-liquefaction results on a coal-alone basis and the results using only coal in the feed is a measure of the amount of synergism observed during co-liquefaction. The above results indicate that the tire components could have a considerable synergistic effect on the conversion of coal to asphaltenes. The effect could be simply an improved hydrogen-shuttling capability due to the tire product. However, the synergism is more likely to be due to a decrease in the rates of retrogressive reactions following the decrease in the concentration of coal radicals in the presence of tire components. Since SBR and PBR are the major organic constituents of the tire, the synergistic effect is probably due to the radicals shown [5] (by electron spin resonance (ESR)) to be formed by the cracking of these components. Other studies [3,10,11] also support the hypothesis that the major role of tire is to stabilize the coal radicals. Finally, Malhotra and McMillen [6] noted that a solvent in coal liquefaction not only stabilizes the free radicals but also enhances bond scission. Therefore, the presence of SBR and PBR could lead to both radical stabilization as well as the breaking of additional bonds in the coal molecule.

Interestingly, the role of carbon black seems minimal. This was confirmed independently by additional runs using mixtures of coal and carbon black – it was found that the product slate was not altered by the addition of carbon black to the coal. This is counter to previous results [1] that carbon black (with elemental sulfur added) promotes the conversion of Illinois No. 6 coal (to methylene chloride-soluble material) at 425°C for a 60 min run. However, Tang and Curtis [12] observed that carbon black (with sulfur added) shows some activity for the liquefaction of Illinois No. 6 coal, but only after the carbon black is heat-treated in N_2 at 560°C. The present study has been carried out under conditions somewhat different from those described above. Most importantly, the coal used here is DECS-6 which has a lower iron content (0.3%) compared to Illinois No. 6 coal (2.8%). In a later work, Farcasiu [13] observed that the activity of carbon black is specific to its method of manufacture. This could explain the variable results regarding the role of carbon black in co-liquefaction.

3.4. *Co-liquefaction of entire tire and coal*

3.4.1. *Effect of temperature and tire/coal ratio*

The effects of tire/coal ratio, R_{TC}, on co-liquefaction are shown at various temperatures in Fig. 4. As in Section 3.3, the results are based on coal alone, i.e., the contribution of the tire has been subtracted out.

At the highest temperature used, 400°C, the effect of the tire on coal conversion is more significant at low values of R_{TC}. There seems to be a slight maximum in the conversion at $R_{TC}\approx 3$. The oil+gas yield decreases more-or-less linearly with an increase in the value of R_{TC}. A comparison of these results with those from Section 3.3 indicates that the synergistic effect of the entire tire is smaller than that of the tire components. This is not surprising since the tire is not merely a physical mixture of the components. In particular, the structure of tire rubber is different from those of the SBR and PBR components used: the tire rubber is highly cross-linked, due to vulcanization reactions with sulfur [10,11]. Also, the accelerators and other "miscellaneous" components not used in the runs with tire components may have an effect. Furthermore, using the Tire-1 sample, Liu et al. [2] observed that the (coal-alone) conversion under the same experimental conditions increases steadily with R_{TC}, i.e., there is no maximum. This indicates that the synergistic effect of tire may be dependent on the composition of tire.

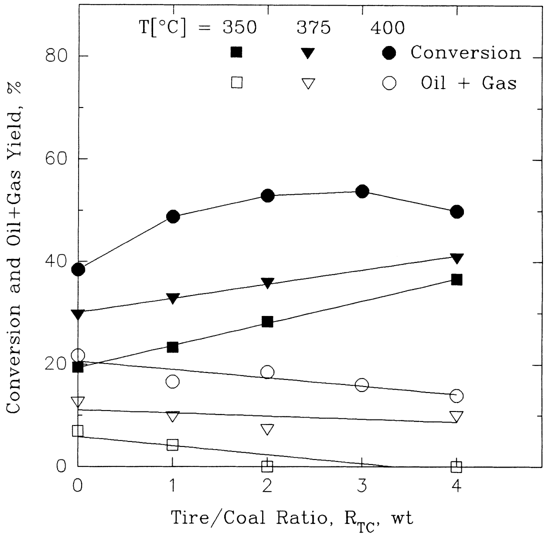

Fig. 4. Effect of temperature and tire/coal ratio on conversion and yield (coal-alone basis) in thermal runs. Reaction conditions are the same as in Fig. 1.

The results at 350°C and 375°C, also in Fig. 4, show that the conversion on a coal-alone basis increases almost linearly with R_{TC} at these lower temperatures, with no apparent maximum. The (coal-alone) yield of the oil+gas fraction decreases with increasing R_{TC}. At 350°C, the yields of oil+gas are negligible at high R_{TC}, suggesting again that, in coal liquefaction, oil+gas is mainly a secondary product. The lower yields of oil+gas in the co-liquefaction runs (compared to those in coal-only runs) suggest again that the coal radicals in the asphaltene range are stabilized relatively quickly by the tire, before their recombination or conversion to oil+gas. Further, the use of the tire in the stabilization of asphaltene radicals can be seen to decrease the yield of tire-derived oil+gas.

The yields of asphaltenes in the co-liquefaction runs are not explicitly noted in Fig. 4, but can be deduced from Eq. (3b). These values (on a coal-alone basis) are much higher than those in the coal-only runs. This is consistent with the hypothesis that the main role of the tire is to stabilize the coal free radicals, which are in the asphaltenic range. As noted earlier, the tire may also promote bond-scission in coal molecules, leading to larger amounts of asphaltenes.

It is interesting to compare the effect of the tire as a solvent to effects reported in the literature using conventional solvents. Using tetralin [3] (a hydrogen donor) or phenanthrene [14] (a hydrogen-shuttler) as solvents results in higher coal conversions than those with the tire. This suggests that the hydrogen-donor and hydrogen-shuttling properties of the tire are weak. This may be due to the "non-fluid" nature of the tire products, which have been noted to consist basically of carbon-black particles surrounded by an oily liquid. However, the conversions of coal with tire are higher than those obtained earlier [3] for coal with hexadecane. The latter conversions are similar to those in the absence of a solvent, i.e., the addition of hexadecane has no effect on coal conversion. This shows that the tire is superior to hexadecane, and that the synergism due to the tire is not merely the physical effect of the heated tire acting as a liquid. Since the tire material is more diverse than the above solvents, it may have multiple roles in coal liquefaction, including radical-stabilization and hydrogen-shuttling.

3.4.2. *Effect of* H_2 *pressure*

Fig. 5 shows the effect of H_2 pressure on conversion and product yields from co-liquefaction at 400°C. In these runs, R_{TC} was kept constant at 1. As before, the conversion and yields are calculated on a coal-alone basis. Hence these values can be compared to those from the runs with only coal.

The conversion in Fig. 5 increases almost linearly from about 35% in the absence of hydrogen to 55% at the H_2 pressure of 1500 psi (cold). This increases the yields of both asphaltenes and oil+gas by about 10 percentage points each. Comparing these results to those from coal (Fig. 3), the slopes of the lines, i.e., the effects of hydrogen pressure, are greater in the co-liquefaction runs than in the coal-only runs. In other words, the synergistic effect of the tire appears to depend on H_2 pressure. This may be due to the increased contribution of the tire to hydrogen-shuttling. Another possibility is that some of the asphaltene radicals which are stabilized by the tire undergo further cracking to produce relatively smaller radicals which are then stabilized by hydrogen.

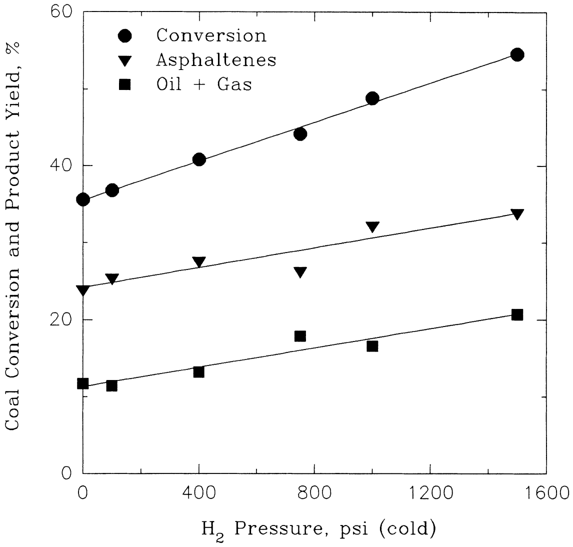

Fig. 5. Effect of H_2 pressure on thermal co-liquefaction of coal and tire. Results are on a coal-alone basis. Reaction conditions are: 400°C, 30 min, R_{TC}=1.

The (coal-alone basis) yields of asphaltenes in the co-liquefaction runs are almost double those in the coal-only runs. On the other hand, the (coal-alone basis) yields of oil+gas in the co-liquefaction runs are lower than those in the coal-only runs at low hydrogen pressures, while the yields are comparable at the highest hydrogen pressure. These results suggest that both the gaseous hydrogen and the tire radicals are used in the stabilization of coal radicals that are in the asphaltenic range. However, the contribution of tire radicals to the stabilization of asphaltenic-range radicals seems higher than the contribution of hydrogen. On the other hand, coal radicals in the oil range are probably stabilized mainly by the hydrogen, and the role of the tire in the formation of oil product would seem to be small.

Using the Tire-1 sample, Liu et al. [2] observed that the H_2 pressure has little effect on co-liquefaction results above 500 psi. As mentioned before, the "oxygen" content of the Tire-1 (as measured by the ultimate analysis, Table 2) is lower than that of the sample used in this study. Perhaps this plays a role in determining the effect of hydrogen in co-liquefaction. It seems that the hydrogen requirements are dependent on the composition of the tire sample.

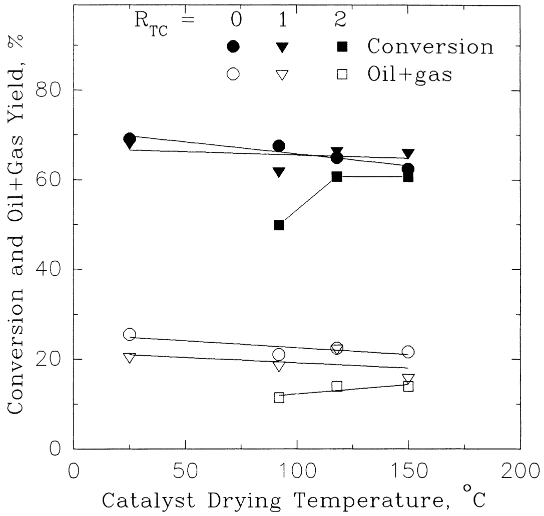

Fig. 6. Effect of catalyst drying temperature on conversion and yield (coal-alone basis). Reaction conditions are: 400°C, 1000 psi H_2 (cold), 30 min. The corresponding thermal values for conversion and oil+gas yield (on coal-alone basis) are 38.4%, 21.7% (R_{TC}=0); 48.8%, 16.7% (R_{TC}=1); 52.9%, 18.5% (R_{TC}=2), respectively.

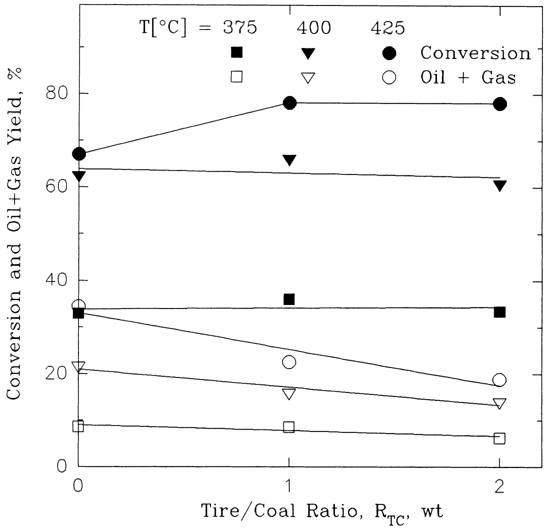

Fig. 7. Effect of reaction temperature and tire/coal ratio on conversion and yield (coal-alone basis) in the catalytic runs. Reaction conditions are: 1000 psi H_2 (cold), 30 min, catalyst drying temperature=150°C.

3.5. *Catalytic runs*

3.5.1. *Effect of catalyst preparation conditions*

The catalytic runs were made using a ferric-sulfide-based catalyst impregnated in situ in the coal. The catalyst loading was 1.67% by weight, based on daf coal. The impregnated coal was dried overnight in N_2 under vacuum at various temperatures.

Fig. 6 shows the effect of the drying temperature of the catalyst and R_{TC} on catalyst performance when the liquefaction is carried out at 400°C. The conversions (on a coal-alone basis) are higher than those in the thermal runs. However, the oil+gas yields are similar to those in thermal runs. The above results show that the catalyst has a high activity for the liquefaction of coal to asphaltenes, even without a solvent. The catalyst drying temperature has only a small effect on the conversion and is probably related to the changes in its pyrrhotite/pyrite (PH/PY) ratio with temperature [15]. Accordingly, all further catalytic runs were made with the catalyst dried at 150°C.

3.5.2. *Effect of tire/coal ratio and temperature in catalytic runs*

Fig. 7 shows the effect of R_{TC} on conversion and yield in catalytic runs at liquefaction temperatures of 375–425°C. This temperature range was used here since the incremental conversion due to catalyst was small at 350°C. At higher temperatures, a larger number of coal radicals may be generated, and these may help utilize the catalyst more effectively.

In the absence of the tire (R_{TC}=0), the conversion of coal in the catalytic runs increases rapidly from 33 wt% at 375°C to over 65 wt% at 425°C. These values are considerably higher than those in the thermal runs, and are comparable to those with solvents such as tetralin [3]. The increase in conversion may be due to increased use of gaseous hydrogen in the presence of catalyst [16]. In the thermal runs with coal, the major source of hydrogen is the coal itself, with a small contribution by gaseous hydrogen [9]. Since coal can supply only a limited amount of hydrogen, the conversions are low. The oil+gas yields in catalytic runs are similar to those in the thermal runs, suggesting that the activity of the catalyst for oil+gas formation is low. The oil+gas yield increases with temperature. As indicated later by the data analysis, this is due to the increase in the conversion of coal with temperature.

The oil+gas yield (coal-alone basis) decreases monotonically with an increase in R_{TC}, especially at high temperatures. The addition of tire does not significantly affect the conversions of coal at 375°C and 400°C. However, at 425°C, the conversion (coal-alone basis) at $R_{TC}=1$ is slightly higher than in the absence of tire. This is interesting since it shows that the combination of a catalyst and an inexpensive waste material as solvent results in conversions almost as high as that obtained with a more expensive hydrogen-donor.

As the value of R_{TC} increases above 1, the coal conversions remain essentially constant. This indicates that the radical stabilization and hydrogen-shuttling due to the tire are overwhelmed by the high catalytic activity. Hence, high R_{TC} values are not particularly beneficial for coal liquefaction.

3.6. Data analysis

In this section, we attempt to quantify the above experimental results by considering simple model involving the liquefaction of tire alone, coal alone and the incremental reaction occurring when tire and coal are co-liquefied. Non-catalytic (thermal) and catalytic reactions are considered to occur in parallel.

3.6.1. Kinetic model

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

$$\mathrm{TR} \xrightarrow{k_{\mathrm{tr}}} \mathrm{OG} \quad (\text{Reaction (i)}). \tag{5}$$

Both the gaseous hydrogen and the catalyst have a negligible effect on the rate of Reaction (i).

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

$$\mathrm{C} \xrightarrow{k_{\mathrm{t}}} \mathrm{A} \quad (\text{Reaction (ii)}), \tag{6a}$$

$$\mathrm{A} \xrightarrow{k_{\mathrm{a}}} \mathrm{OG} \quad (\text{Reaction (iii)}). \tag{6b}$$

It should be noted that the oil and gas products are "lumped" together as OG, since their yields show a similar dependence on the process conditions. Also, the gas yields are generally small (<5%). The reverse reaction of asphaltenes-to-coal is neglected due to the relatively mild temperatures used in this study.

In the presence of the catalyst, a significant fraction of the coal is liquefied using gaseous hydrogen according to the reaction:

$$\mathrm{C} \underset{(\mathrm{H_2,\,catalyst})}{\xrightarrow{k_{\mathrm{c}}}} \mathrm{A} \quad (\text{Reaction (iv)}), \tag{7a}$$

$$\mathrm{A} \underset{(\mathrm{H_2,\,catalyst})}{\xrightarrow{k_{\mathrm{ac}}}} \mathrm{OG} \quad (\text{Reaction (v)}). \tag{7b}$$

Curtis et al. [16] used a similar reaction scheme for the liquefaction of Illinois No. 6 coal over a commercial NiMo/Al_2O_3 catalyst at 400°C using 1-methylnaphthalene as the solvent.

In the presence of the tire (TR), the conversions increase, probably due to the synergism by the free-radical reactions between coal and tire, as well as due to the increased hydrogen-shuttling. For the thermal case, the synergism reaction is represented by:

$$\mathrm{C} + \mathrm{TR} \xrightarrow{k_{\mathrm{s}}} \mathrm{A} \quad (\text{Reaction (vi)}). \tag{8}$$

In the presence of the catalyst, a coal-tire-catalyst synergism reaction may be occurring:

$$\mathrm{C} + \mathrm{TR} \underset{(\mathrm{H_2,\,catalyst})}{\xrightarrow{k_{\mathrm{sc}}}} \mathrm{A} \quad (\text{Reaction (vii)}). \tag{9}$$

The experimental data suggest that the extent of synergism is dependent on the concentration of tire. Note that, in the model, the effect of tire on oil+gas yield in co-liquefaction runs is taken into account indirectly.

Now the rate of tire conversion, r_{tr}, can be obtained by combining Reactions (i), (vi) and (vii):

$$-r_{\mathrm{tr}} = k_{\mathrm{tr}}C_{\mathrm{tr}}^2 + (k_{\mathrm{s}} + k_{\mathrm{sc}})C_{\mathrm{tr}}C_{\mathrm{c}}, \tag{10}$$

where k_{tr}, k_{s} and k_{sc} are the rate constants for Reactions (i), (vi) and (vii), respectively, and C_{c} and C_{tr} represent the mass fractions of coal (THF-insolubles) and tire. Similarly the rate of coal conversion, r_{c}, can be obtained by combining Reactions (ii), (iv), (vi) and (vii):

$$-r_{\mathrm{c}} = (k_{\mathrm{t}} + k_{\mathrm{c}})C_{\mathrm{c}}^2 + (k_{\mathrm{s}} + k_{\mathrm{sc}})C_{\mathrm{tr}}C_{\mathrm{c}}. \tag{11}$$

Here, k_t and k_c are the rate constants for Reactions (ii) and (iv), respectively. Further, the rate of formation of asphaltenes, r_a, is:

$$r_a = (k_t + k_c)C_c^2 + (k_s + k_{sc})C_{tr}C_c - (k_a + k_{ac})C_a^2, \qquad (12)$$

with k_a and k_{ac} being the rate constants for Reactions (iii) and (v), and C_a the mass fraction of asphaltenes.

In Eqs. (10)–(12), we implicitly assume a second-order dependency overall for reactions involving tire alone and coal alone. Such a model has been used earlier for coal by Liu et al. [3] and Furlong et al. [17]. The use of second-order kinetics to describe a series of parallel first-order reactions has been discussed by Aris [18] and by Weekman [19]. For the synergistic reactions (vi) and (vii), we assume the kinetics are second-order overall, but are first-order in each of the coal and tire. In this way, all the reactions are considered as second order. It should be noted that the dependency of reaction rate on hydrogen pressure is not explicitly shown in Eqs. (10)–(12) since all the data used in the analysis were obtained at a H_2 pressure of 1000 psi (cold). Also, transport limitations in and around the catalyst particles are not considered, i.e., observed rate constants are used. In any case, the catalyst particle has been shown earlier [3] to be small, of size around 18 nm.

The data for only tire, the data for only coal, and the coal/tire co-liquefaction data were analyzed separately, as described below. In order to minimize the correlation between the activation energy and the pre-exponential factor, each of the rate constants k was re-parametrized to the form:

$$k = k(M)\exp[E\{1/T(M) - 1/T\}/R]. \qquad (13)$$

Here $k(M)$ is the value of k at $T(M)$, which was taken as 673 K. The values of $k(M)$ and the activation energy E, along with their 95% confidence limits, are shown in Table 3.

3.6.2. *Data for only tire and only coal*

Taking C_c as zero and integrating Eq. (10) leads to

$$X_{tr}/(1 - X_{tr}) = k_{tr}C_{to}t, \qquad (14)$$

where X_{tr} is the conversion of tire at time t and C_{to} is the initial mass fraction of the tire. Substituting the data for only tire (thermal reaction) from Fig. 1 in Eq. (13) and Eq. (14) yields the best-fit values of and E_{tr} as shown in Table 3.

Table 3
Summary of kinetic results[a]

Rate constant	$k(M)$[b] (h^{-1} mf^{-1})[c]	Activation energy (kJ mol^{-1})
k_{tr}	4.0±1.1	24.4±6.9
k_t	1.0±0.4	35.7±7.2
k_c	1.2±0.8	158.4±122.4
k_a	6.8±1.8	0
k_{ac}	0	0
k_s	3.6±0.6	83.8±27.4
k_{sc}	0	0

[a] ± Represents 95% confidence limits.
[b] Value of k at $T(M)$=673 K.
[c] mf=mass fraction.

Similarly, substituting the data of Fig. 2 in the integrated form of Eq. (11) with C_{tr} set equal to 0 allows us to estimate the value of the kinetic parameters $k_t(M)$ and E_t for thermal liquefaction of $k_{tr}(M)$ only coal. These values are also shown in Table 3.

Values of the catalytic parameters $k_c(M)$ and the activation energy, E_c, for only coal were obtained by using data on overall conversion from Fig. 7 with R_{TC}=0, then subtracting the known value for the thermal reaction rate. Note that the value of $k_c(M)$ shown in Table 3 corresponds to a catalyst loading of 1.67 wt% daf coal. The confidence limits on $k_c(M)$ and E_c are rather large. This may be due to the small number of data points in the runs with only coal. Also, the values of k_c are affected by the error bars in k_t.

The parameters for the thermal and catalytic conversion of asphaltenes to oil and gas were calculated in an analogous manner, except that the corresponding rate expression, Eq. (12), was integrated numerically rather than analytically. The thermal values $k_a(M)$ and E_a were calculated as 15.5±5 h^{-1} mf^{-1} and 10.6±14.2 kJ mol^{-1}, respectively. With these values, the values of $k_{ac}(M)$ and E_{ac} were found to be −11.7±7 h^{-1} mf^{-1} and 34.3±109.5 kJ mol^{-1}. These results indicate that the values of E_a, E_{ac} and $k_{ac}(M)$ are not significantly different from zero. In other words, the rate of asphaltene conversion to oil+gas is not significantly altered by the catalyst or the temperature. This is consistent with the experimental data in Fig. 2. Accordingly, the thermal and catalytic data were re-analyzed with E_a, k_{ac} and E_{ac} all set equal to zero. The final value of $k_a(M)$ is shown in Table 3.

3.6.3. *Coal+tire co-liquefaction data*

In this case, Eqs. (10)–(12) were integrated numerically to obtain values of the thermal and catalytic parameters of the synergism reactions, k_s and k_{sc}, respectively. Note that the experimental data used were the *overall* conversions and yields from co-liquefaction, corresponding to those on the coal-alone basis shown in Figs. 4 and 7.

From the thermal data of Fig. 4, values of $k_s(M)$ and E_s were calculated as $3.56\pm0.74\ \mathrm{h^{-1}\ mf^{-1}}$ and $83.5\pm27.9\ \mathrm{kJ\ mol^{-1}}$. From the catalytic data of Fig. 7, values of $k_{sc}(M)$ and $E_s(M)$ were calculated as $0.62\pm1.3\ \mathrm{h^{-1}\ mf^{-1}}$ and $191.0\pm388.5\ \mathrm{kJ\ mol^{-1}}$, not significantly different from zero. This suggests that the catalyst has a negligible effect on tire synergism, i.e., that the rate of Reaction (vii) is negligible compared to the rate of Reaction (vi). Hence, k_{sc} was set equal to zero, and k_s was re-calculated using both the thermal and catalytic data. The values of $k_s(M)$ and E_s are given in Table 3.

3.6.4. *Discussion of reaction scheme*

The experimental values of overall conversion (of coal+tire) and overall yield (of oil+gas) are compared in Fig. 8 with the values calculated from the parameters of Table 3. 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. In thermal runs, the predicted overall conversion (X_{OV}) increases with the addition of tire, to a maximum of about 65%, compared to 62% observed experimentally. In catalytic runs, the model predicts a maximum overall conversion of 72%, as observed experimentally. Also, 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.

The data analysis provides some interesting comparisons. For example, at 400°C, the value of the rate constant, k_s, for the synergism reaction, i.e., Reaction (vi), is nearly four times that of the thermal rate constant, k_t, for Reaction (ii). Since the activation energy for the former is larger than that for the latter, the difference between the rate constants will increase even further at higher temperatures. Therefore, the rate of Reaction (vi) (for example, at a tire/coal ratio of 1) is higher than the rate of Reaction (ii). In other words, the free-radical reactions between coal and tire are relatively fast in the thermal runs.

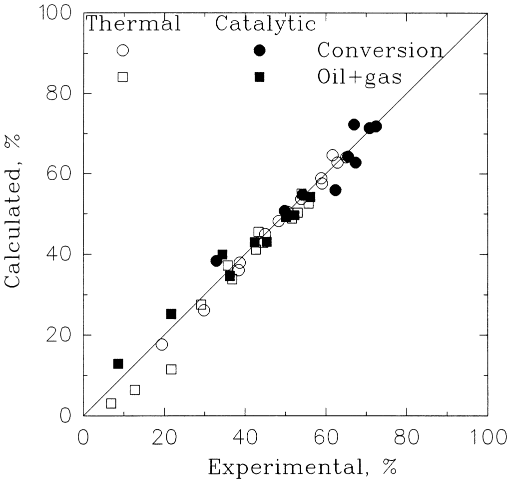

Fig. 8. Comparison of the experimental and calculated values of the overall conversions and oil+gas yields from coal/tire co-liquefaction.

At 400°C, the value of the catalytic rate constant, k_c, is higher than that of the thermal rate constant k_t. Further, the catalytic liquefaction of coal has a high activation energy relative to the value for the thermal liquefaction. This indicates the absence of any inter- or intra-particle transport limitations for catalytic liquefaction, which is consistent with the small size of the catalyst particles. The low E_t value indicates that thermal liquefaction could be subject to strong pore diffusion or hydrogen-transfer limitations in the absence of a hydrogen-donor solvent.

Interestingly, the activation energy for Reaction (iii), E_a, is not significantly different from zero. This suggests that the increase in oil+gas yield at high temperatures is not due to an increase in k_a but rather to an increase in the amount of asphaltenes. Further, the overall yield of oil+gas increases in the presence of tire due to increase in the tire conversion. However, the oil+gas yields on a coal-alone basis decrease in the presence of tire. Perhaps the tire components cap the coal radicals in the asphaltene range relatively quickly, before the coal radicals can react further to oil or gas.

It is difficult to compare the present results with those in the literature, due to the differences in the type of coal and other process conditions such as solvent and catalyst. However, it seems that simple reaction schemes, such as Eqs. (5),(6a),(7a)–(9), may be adequate for correlating the coal/tire co-liquefaction data from both thermal and catalytic runs at various temperatures and tire/coal ratios.

4. Conclusions

The conversion and product yields from coal-only and tire-only feeds increase with increase in temperature but the effect of temperature is more pronounced for the case of the coal than for the tire. The product yields are not affected significantly by the changes in hydrogen pressure.

The synergism between tire and coal during co-liquefaction can be quantified by comparing conversions and yields (calculated on a coal-alone basis) with the corresponding parameters using only coal as the feed. Co-liquefaction of tire with coal provides a considerable synergistic effect on the conversion and yield of asphaltenes. However, the synergistic effect of the entire tire is lower than that of its components SBR and PBR. The synergism due to the tire increases with increase in temperature and hydrogen pressure, at least up to a tire/coal ratio of 3. The synergism is probably due to enhanced radical-stabilization and the hydrogen-shuttling in the presence of tire.

The addition of a ferric-sulfide-based catalyst increases the coal conversion significantly in the absence of tire. The catalytic effect is attenuated slightly by the addition of tire. However, the oil yields are not altered significantly by the use of the catalyst.

A consecutive reaction scheme for the conversion of coal to asphaltenes and oil+gas represents the data from both thermal and catalytic runs 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. The model verifies and quantifies the observations noted above.

Acknowledgements

This work was conducted under US Department of Energy Contract No. DE-FC22-90PC90029 under the cooperative Agreement to the Consortium for Fossil Fuel Liquefaction Science. The authors are grateful to Dr. M. Farcasiu of Pittsburgh Energy Technology Center for providing the tire components.

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