

COAL-TIRE CO-LIQUEFACTION

Ramesh K. Sharma, Dady B. Dadyburjor, John W. Zondlo,
Zhenyu Liu and Alfred H. Stiller
Department of Chemical Engineering
West Virginia University
P.O. Box 6102, Morgantown WV 26506-6102

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ABSTRACT

Co-liquefaction of ground coal and tire rubber was studied at 400°C both with and without catalyst. Two different tire samples were used. In the non-catalytic runs, the conversion of coal increased with the addition of tire and the increase was dependent on tire/coal ratio and hydrogen pressure. Using a ferric sulfide-based catalyst, the coal conversion increased with an increase in the catalyst loading. However, the increase was more pronounced at loadings of around 0.5 wt%. The addition of tire to coal in the catalytic runs was not particularly beneficial, especially, when the tire/coal ratio was above 1.

INTRODUCTION

Disposal of used 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]. Liu et al. [1] studied the co-liquefaction of tire and DECS-6 coal. The tire sample was prepared from an used Goodyear Invicta tire. When the tire and coal were co-liquified at 400°C it was observed that the conversion of coal increased in the same way as with the addition of tetralin (a good hydrogen donor solvent) to coal. Similar results were obtained by Farcasiu and Smith [2] for the liquefaction of tire and Illinois No. 6 coal at 425°C. In both these studies a complete conversion of tire was obtained.

In this work, the effect of H₂ pressure and tire/coal ratio on the co-liquefaction of tire and coal was studied at 400°C. Two different tire samples were used. Runs were made with tire and coal separately as well as using tire-coal mixtures with tire/coal ratios of 0.4. The hydrogen pressure was varied between 0-1500 psi (cold). Experiments were also done using a ferric sulfide-based catalyst at loadings of up to 1.67 wt% based on coal.

EXPERIMENTAL

The coal used was DECS-6 which is a high-volatile-A bituminous coal from the Blind Canyon seam in Utah. Two different tire samples were used. The first sample was prepared from a Goodyear Invicta tire, recycled in-house at WVU (Tire-1). The other 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 Tire-1 contained 67 wt% volatile matter (on a dry, ash-free basis) and 33 wt% fixed carbon while Tire-2 contained 71 wt% volatile matter and 29 wt% fixed carbon. The fixed carbon essentially represents the content of carbon black in the tires. The amounts of volatile matter and fixed carbon in coal were 49 wt% and 51 wt%, respectively.

The experimental equipment, run procedures and analytical techniques have been described earlier [1] and are given briefly. 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 H₂ or helium to the desired pressure. The feed consisted of tire or coal or a mixture of the two in different ratios. In the catalytic runs, the catalyst was impregnated in-situ on the coal. 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 HS fraction was used to recover the 'oil fraction'. The THF-soluble/hexane-insoluble fraction, i.e. the HI fraction, represents asphaltenes. The conversion (X) and the yield of asphaltenes (A) were calculated as follows:

$$X = (F_m - TI) / F_{daf} \quad (1)$$

$$A = HI / F_{daf} \quad (2)$$

where F_m and F_{daf} represent the amount of feed on moisture-free and 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:

$$O = X - A - G \quad (3)$$

In many cases, the combined oil + gas yield was calculated by difference. Most runs were made in duplicate and the experimental error was $\pm 2.5\%$.

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;

$$X_{cm} = (X_{ov} - w_t x_t) / w_c \quad (4)$$

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 (4), x_{cm} is the estimated conversion of coal in the mixture and x_t is the conversion of tire which was assumed to be the same as in tire-alone runs. The yield of oil + gas from coal was estimated similarly. The asphaltenic yield from coal was calculated by difference. It should be recognized that the conversion of tire in the co-liquefaction runs may be different from that in tire-alone runs. However, the above assumptions were made simply to 'lump' the entire incremental effect into a single component, i.e., coal.

RESULTS AND DISCUSSION

Effect of Hydrogen Pressure

The effect of hydrogen pressure on the product slate from coal-alone and tire-alone (Tire-2) was studied at 400°C. The runs at zero hydrogen pressure were made using 1000 psi (cold) helium. The effect of hydrogen pressure on the tire conversion was found to be minimal. Also, the hydrogen pressure affected the coal results only slightly. The conversion of coal increased with increase in hydrogen pressure, resulting in an increase in the yields of both asphaltenes and oil+gas fractions. At all the pressures, the yield of asphaltenes was lower than that of oil plus gas. Thus it appears that the gaseous hydrogen is necessary to stabilize the coal radicals. This is consistent with the observations of Malhotra and McMillen [3] and Whitehurst et al. [4] that the retrogressive reactions in coal liquefaction become more pronounced under hydrogen-deficient conditions. The results indicated that the relative contribution of hydrogen to the stabilization of asphaltenic radicals is somewhat greater than to the radicals in the oil range.

Figures 1 and 2 show the effect of hydrogen pressure in the co-liquefaction runs using Tire-1 and Tire-2, respectively. The tire/coal ratio was unity. The conversion and oil + gas yield from tire were assumed to be the same as those for the liquefaction of tire alone and the results are reported on coal-alone basis. It is seen that, with Tire-1 (Figure 1), both the conversion and oil+gas from coal increase with an increase of H_2 pressure, up to around 500 psi (cold). At higher H_2 pressures, the results are relatively insensitive to the pressure. However, when Tire-2 was used, the conversion of coal increased monotonically with the H_2 pressure (Figure 2). This led to increase in the yields of both asphaltenes and oil+gas. When these results were compared to those for the coal alone, it was found that the effect of hydrogen pressure on the product slate is greater in the co-liquefaction runs than in the coal-alone runs. The synergistic effect of Tire-2 also appears to depend on H_2 pressure, i.e. there is an increased synergism at high hydrogen pressures. The yields of asphaltenes in the co-liquefaction runs (Figure 2) are almost double those which were observed in the coal-alone runs. On the other hand, the yields of oil+gas are lower compared to those in coal-alone runs, especially at low hydrogen pressures. This indicates that both the gaseous hydrogen and the tire radicals are used in the stabilization of coal radicals that are in the asphaltenic range. Further, the contribution of tire to the radical stabilization and bond scission is considerably higher compared to that of hydrogen. In contrast, the coal radicals in oil range are probably stabilized mainly by the hydrogen and the addition of tire seems to have little effect especially at low hydrogen pressures.

Effect of Tire/Coal Ratio

The effect of tire/coal ratio on conversion and product yields using Tire-1 is shown in Figure 3. As before, the results are based on coal, i.e. the contribution of tire has been subtracted out. The conversion of coal increases from around 35 wt% in the absence of tire to over 65 wt% when the tire/coal ratio was 4. The yield of oil+gas appears to be independent of tire/coal ratio. Similar results were obtained with Tire-2 where the effect of tire addition was found to be more significant at low tire/coal ratios (Figure 4). The conversion of coal increases from 38 wt% (coal-alone runs) to 49 wt% at tire/coal ratio of 1. At higher ratios, the addition of tire has only a small effect on coal conversion. There seems to be a slight maximum in the conversion at tire/coal ratio of 3 where the conversion was 54 wt%. The oil yield for the co-liquefaction may be maximum at a tire/coal ratio of 2.

Effect of Using Ferric Sulfide-based Catalyst

The catalytic runs were made using catalyst based on iron sulfide, Fe_2S_3 . The catalyst was impregnated *in-situ* on the coal. The coal was first mixed with a dilute aqueous solution of Na_2S and agitated vigorously before adding $FeCl_3$ solution. The suspension containing coal and catalyst was filtered, washed and dried in N_2 under vacuum.

Figure 5 shows the effect of catalyst loading on the conversion and product yield. In these runs, Tire-1 was used and the tire/coal ratio was 1. Again, the results are based on coal. The conversion of coal increases from around 45 wt% in the absence of catalyst to over 80 wt% when the catalyst loading was 1.67 wt%. The yield of oil+gas increased from 10 wt% to 20 wt%. This indicates that the increased loading is beneficial to the activity and selectivity of the catalyst. However, the incremental effect of catalyst loading is more pronounced at loadings of around 0.5 wt%.

The effect of tire/coal ratio on the conversion and product yields in the catalytic runs is presented in Figure 6. These runs were made with Tire-2 and the catalyst loading was 1.67 wt%. The addition of tire appears to have only a small effect on the conversion and product yields below a tire/coal ratio of 1. At higher ratios, both the conversion and yields decrease indicating that the addition of excess tire is detrimental to the activity of the catalyst. This may be due to the poisoning of the catalyst by the polymeric compounds present in the tire rubber.

CONCLUSIONS

1. The co-liquefaction of tire rubbers with coal has a considerable synergistic effect on the conversion and product yields from coal.
2. The synergism due to the addition of tire increases with an increase in hydrogen pressure and tire/coal ratio.
3. The conversion and product yields from coal increase using ferric sulfide-based catalyst. However, the synergistic effect of tire in the catalytic runs is small, especially, at high tire/coal ratios where the conversion and yields actually decrease.

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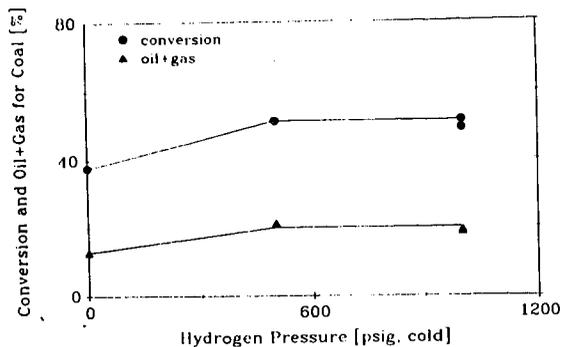


Figure 1. Effect of H_2 pressure on conversion and yields of coal in a coal/tire mixture. Conditions: $400^\circ C$, 30 min, tire/coal = 1. Tire-1 and DECS-6 coal were used.

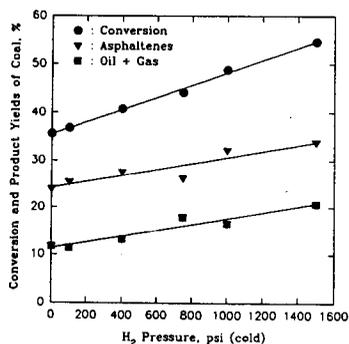


Figure 2. Effect of H_2 pressure on conversion and yields of coal in a coal/tire mixture. Conditions: same as in Figure 1. Tire-2 and DECS-6 coal were used.

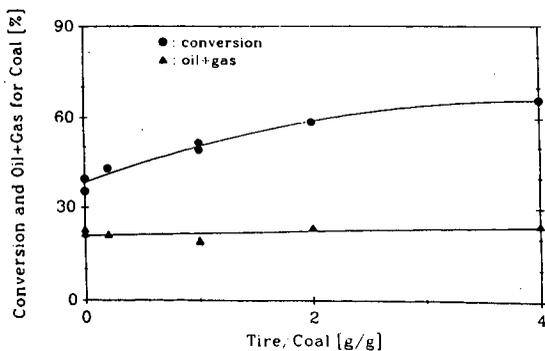


Figure 3. Effect of tire/coal ratio on conversion and yield of coal in a coal/tire mixture. Conditions: $400^\circ C$, 30 min, H_2 pressure = 1000 psi (cold). Tire-1 and DECS-6 coal were used.

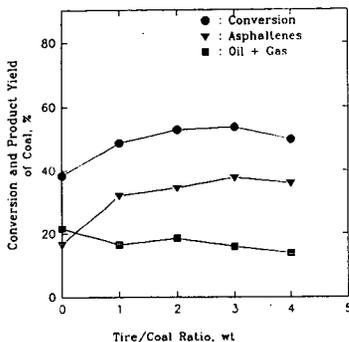


Figure 4. Effect of tire/coal ratio on conversion and yield of coal in a coal/tire mixture. Conditions: Same as Figure 3. Tire-2 and DECS-6 coal were used.

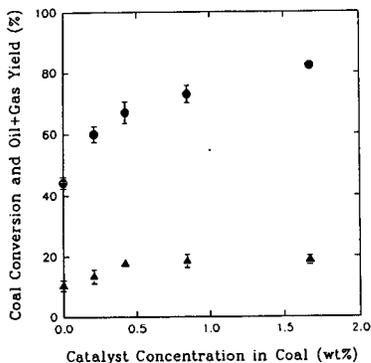


Figure 5. Effect of catalyst loading on conversion and yield of coal in a tire/coal mixture. Conditions: same as in Figure 3. Tire-1 and DECS-6 coal were used.

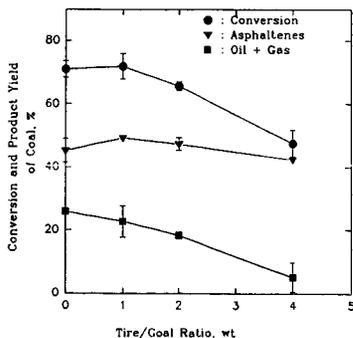


Figure 6. Effect of tire/coal ratio on conversion and product yields of coal. Conditions: 400°C, 30 min, 1000 psi (cold), 1.67% catalyst loading. Tire-2 and DECS-6 coal were used.