

## TWO STAGE CATALYTIC LIQUEFACTION OF COAL AND WASTE TIRE

Ramesh K. Sharma, Dacheng Tian, John W. Zondlo  
and Dady B. Dadyburjor

Department of Chemical Engineering  
West Virginia University

P.O. Box 6102, Morgantown, WV 26506-6102

### INTRODUCTION

Disposal of waste tires is a major environmental problem. Liquefaction of such tires in conjunction with coal was suggested as an alternative for their disposal [1,2]. The addition of tire has a synergistic effect on coal conversion but the synergism decreases in the presence of catalyst at high tire/coal ratios. The synergistic effect is mainly due to the rubber portion of the tire and the effect of carbon black is small. The tire can be liquefied under fairly mild conditions whereas the liquefaction of coal requires relatively more severe conditions. This indicates that optimum conditions for liquefaction of coal and tire are not the same. Further, the simultaneous co-liquefaction of coal and tire has the disadvantage that the carbon black of the tire is essentially lost after the liquefaction since it is mixed with the unreacted coal residue. Hence, a multi-stage process for coal/tire liquefaction may be more appropriate. The first stage of this process is the liquefaction or pyrolysis of tire to obtain tire oil and tire residue (mostly carbon black), and the second stage is the liquefaction of coal with tire oil in the presence of a catalyst. Tang and Curtis [3] studied the two-stage liquefaction of coal and tire using NiMo/Al<sub>2</sub>O<sub>3</sub> as catalyst and observed that the coal conversion was higher than in runs where the coal was co-liquefied with the whole tire.

In this work, two-stage catalytic liquefaction of coal and waste tire was studied using an impregnated ferric sulfide-based catalyst. This was shown to be a superior catalyst for coal liquefaction [4]. The tire was liquefied separately in first stage at 350° or 400°C under N<sub>2</sub> or H<sub>2</sub>. In second stage, coal was liquefied with tire oil (obtained from first stage) at 350-450°C, 1000 psi (cold) H<sub>2</sub>, using various tire oil/coal ratios. The effect of various tire oils, prepared under different conditions, on coal liquefaction was studied. The results are compared to those from single-stage co-liquefaction of coal and tire.

### EXPERIMENTAL

The tire sample was obtained from the University of Utah Tire Bank and represents a mixture of waste, recycled tires ground to -30 mesh. The tire contains 29% fixed carbon which is essentially carbon black. Wyodak coal, which is a sub-bituminous B coal, was used. The coal was dried overnight at -100°C. The dried coal has a moisture-content of <1% and 6.6% ash based on dry, ash-free (daf) coal.

**Liquefaction of Tire in the First Stage.** The liquefaction of tire was performed in first stage using an autoclave. The autoclave was loaded with about 500 g of tire, and was purged and pressurized with N<sub>2</sub> or H<sub>2</sub> to 1000 psi (cold). The autoclave was then heated to the desired temperature of 350° or 400°C and maintained at that temperature for 1h before being cooled. The gaseous products were vented into a hood. The solid and liquid products were washed and extracted with tetrahydrofuran (THF) for 24h. The THF-insoluble material was separated by filtration and represents tire residue. After the removal of THF by rotary evaporation, the THF-solubles were obtained as tire oil. The conversion of tire was ~70% at 400°C, which indicates that the entire organic portion of tire was converted to oil and gas. At 350°C, the conversion was ~53%. The conversions were not affected by the choice of N<sub>2</sub> or H<sub>2</sub>. The various

tire oil samples were designated as Tire oil #1 (prepared at 400°C under H<sub>2</sub>), Tire oil #2 (350°C, H<sub>2</sub>) and Tire oil #3 (350°C, N<sub>2</sub>).

**Liquefaction of Coal and Tire Oil in the Second Stage.** The coal was liquefied with various tire oils (obtained from first stage) at 350-450°C, 1000 psi H<sub>2</sub> (cold) using different tire-oil/coal ratios. The experimental equipment, run procedures and analytical techniques are essentially the same as those described earlier [2]. 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<sub>2</sub> to 1000 psi (cold). The feed consisted of coal and tire-oil in different ratios. The catalyst was impregnated directly in the coal at a loading of 1.67% based on daf coal. The gaseous products were collected and analyzed by gas chromatography. The solid and liquid products in the reactor were analyzed in the same way as the products from the autoclave. The THF-insoluble material (TI) represents the unreacted coal. 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 fractions. The hexane-insoluble fraction (HI) 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<sub>m</sub> and F<sub>daf</sub> represent the amount of coal on moisture-free and 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 most cases, the combined oil+gas yield is reported since the gas yields were usually small (~4.5% at 400°C). The experimental error was ±2%, each, in conversion and asphaltenes yield and ±4% in oil+gas yield.

## RESULTS AND DISCUSSION

**Effect of Preparation Temperature in the First Stage.** Figures 1-3 show the effect of equivalent tire/coal ratio, R<sub>ETC</sub>, on conversion and oil+gas yield at 400°C for various tire oils. R<sub>ETC</sub> represents tire/coal ratio for which the tire-oil/coal ratio is the same as in a given run. For example a tire-oil/coal ratio of 0.66 is equivalent to R<sub>ETC</sub> of 1 since the yield of tire oil from tire at 400°C is ~66%.

As seen in Figure 1, the conversion of coal is low but increases dramatically in the presence of catalyst. The conversion also increases when the coal is liquefied with Tire oil #1. The increase is dependent on the value of R<sub>ETC</sub> in both thermal and catalytic runs. The oil+gas yield in catalytic runs also increases slightly with increase in R<sub>ETC</sub>. The results indicate that the tire oil has a synergistic effect on coal liquefaction. A similar synergism is observed in thermal runs using Tire oil #2 with coal (Figure 2). However, in the presence of catalyst, the synergistic effect of Tire oil #2 is negligible. Essentially similar observations are made with Tire oil #3 (Figure 3), except, in this case, the synergism is seen in both thermal and catalytic runs, as with Tire oil #1. Thus, the synergistic effect of tire oil is dependent on the preparation conditions for tire oil in the first stage. This indicates that the nature or composition of various tire oils may be different. Work is underway to characterize the three oils.

The major problem in first-stage-liquefaction of tire was the recovery of Tire oil #3 since the rate of filtration was extremely low. When a coarse filter was used, the tire oil contained significant concentration of carbon black particles and the

synergistic effect of tire oil on coal liquefaction was relatively small, as in the case of Tire oil #2. Both Tire oil #2 and Tire oil #3 were prepared at 350°C. In addition to the difficulties in the recovery of tire oil at 350°C, another disadvantage of using a low temperature in the first stage is that the conversion of tire at 350°C is low so that a significant fraction of the tire oil is lost to the carbon black-residue. This impedes the easy recycle of the carbon black.

**Effect of Liquefaction Temperature in the Second Stage.** The effect of addition of Tire oil #1 on the results of coal liquefaction at 450°C is presented in Figure 4. The synergism due to tire oil in the absence of catalyst is small. However, in the catalytic runs, both the conversion and yield increase in the presence of tire oil and are highest at  $R_{BTC}=1$ . At the higher  $R_{BTC}$  value, the conversion is essentially the same as at  $R_{BTC}=1$  but the oil+gas yield is lower. This is in contrast to the results at 400°C where both the conversion and yield increased continuously with increase in  $R_{BTC}$ . The results of coal liquefaction at 350°C are not presented since the conversion of coal even in the presence of catalyst and tire oil was low.

**Comparison of Two-Stage Results with Single-Stage Co-Liquefaction of Coal and Tire.** Figures 5 and 6 compare the results of two-stage liquefaction to those from single-stage co-liquefaction of coal and tire. As seen in Figure 5, the conversion and oil+gas yields from two-stage liquefaction are higher than those from single-stage co-liquefaction at 400°C and the difference increases as the value of  $R_{BTC}$  is increased. Essentially similar observations are made at 450°C (Figure 6), except, in this case, the difference between the two-stage and single-stage results is maximum at  $R_{BTC}=1$ . Since the most appropriate value of  $R_{BTC}$ , from commercial point of view, is around 1, the two-stage catalytic liquefaction is particularly beneficial at high temperatures where the conversions are also high.

#### CONCLUSIONS

1. The addition of tire oil has a synergistic effect on coal conversion. In the absence of catalyst, the synergistic effects are similar with various tire oils prepared under different conditions. With catalyst, the synergism is greatest with tire oil prepared at 400°C under  $H_2$ .

2. The synergism due to tire oil increases continuously with  $R_{BTC}$  at 400°C. At 450°C, the maximum synergistic effect is observed at  $R_{BTC}=1$ .

3. The synergistic effect of tire oil is greater than that of the whole tire, especially at high tire-oil/coal ratios. This indicates that the two-stage liquefaction may be preferable to the single-stage co-liquefaction of coal and tire.

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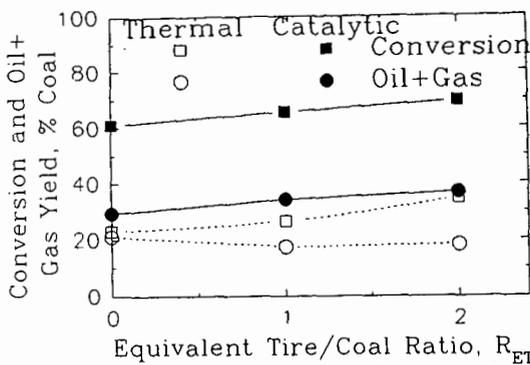


Figure 1. Effect of  $R_{ETC}$  on liquefaction of coal with Tire oil #1. Tire oil preparation conditions: 400°C, 1000 psi (cold)  $H_2$ . Liquefaction conditions: 400°C, 1000 psi  $H_2$  (cold), 30 min, 1.67% catalyst loading.

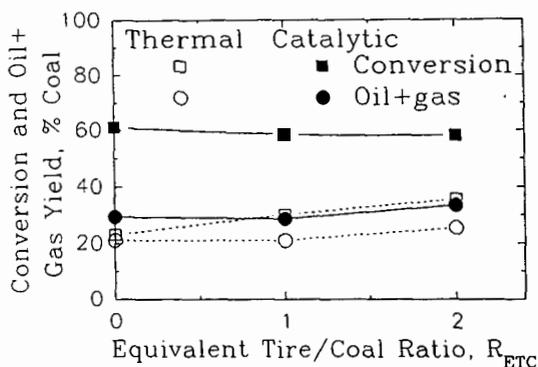


Figure 2. Effect of  $R_{ETC}$  on liquefaction of coal with Tire oil #2. Tire oil preparation conditions: 350°C, 1000 psi (cold)  $H_2$ . Liquefaction conditions are the same as in Figure 1.

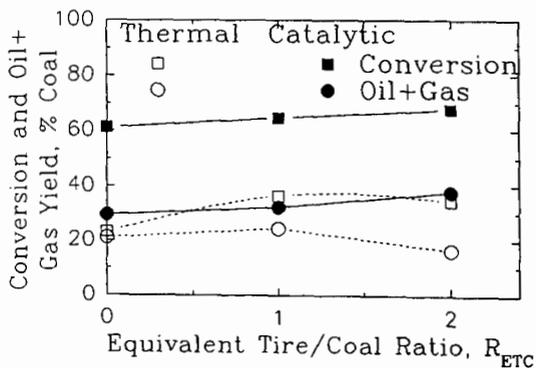


Figure 3. Effect of  $R_{ETC}$  on liquefaction of coal with Tire oil #3. Tire oil preparation conditions: 350°C, 1000 psi (cold)  $N_2$ . Liquefaction conditions are the same as in Figure 1

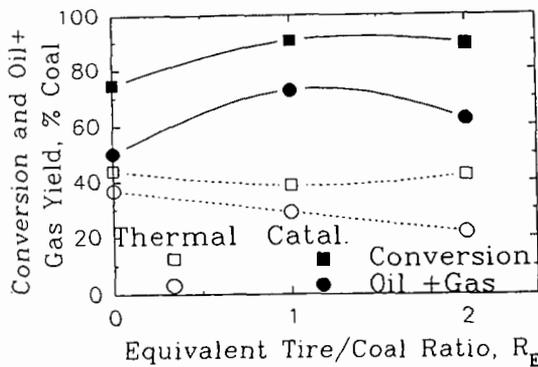


Figure 4. Effect of  $R_{ETC}$  on liquefaction of coal with Tire oil #1. Conditions are the same as in Figure 1, except the liquefaction temperature is 450°C.

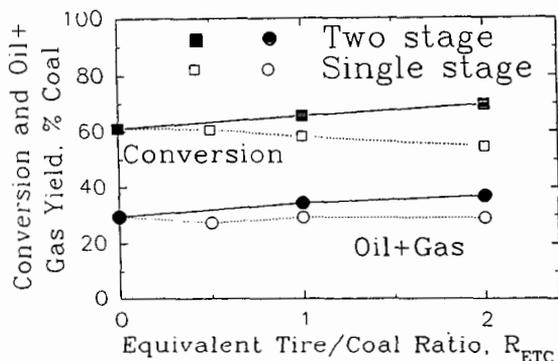


Figure 5. Comparison of two-stage results with single-stage co-liquefaction of coal and tire. Conditions are the same as in Figure 1. Tire oil #1 was used in two-stage and whole tire in single-stage process.

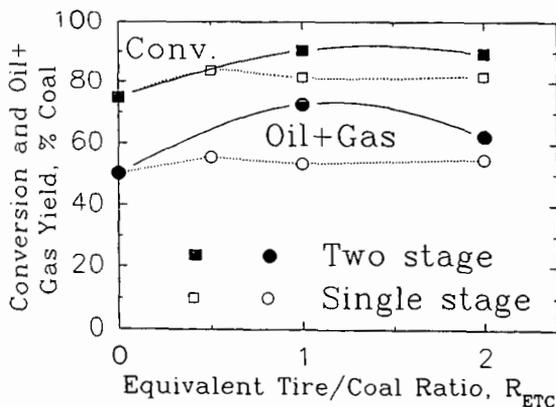


Figure 6. Comparison of two-stage results with single-stage co-liquefaction of coal and tire. Conditions are the same as in Figure 1, except the liquefaction temperature is 450°C. Tire oil #1 was used in two-stage and whole tire in single-stage process.