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Hydropyrolysis of Alberta coal and petroleum residue using calcium oxide catalyst and toluene additive

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Abstract

Hydropyrolysis of a mixture of Alberta coal and Athabasca bitumen was carried out in a batch reactor using calcium oxide as an alternate catalyst and the results were compared with those of widely used iron oxide and well-known NiMo/Al_2O_3 catalysts. Most of the reactions were done at temperatures of 500–540°C, residence time of 1 min and hydrogen pressure of 3.4 MPa. Maximum distillable oil (below 523°C) yield of 55 wt% and pitch conversion of 62 wt% were obtained in the presence of CaO or Fe_2O_3 and these values were higher than those without catalyst, although NiMo/Al_2O_3 catalyst gave much higher oil yield and pitch conversion. Catalyst concentration (above 2 wt%) has no consequence upon the distribution of various product fractions.

In another study, addition of 15% toluene to the feed in the absence of catalyst led to higher distillable oil yield (68 wt%) and pitch conversion (72 wt%) in the hydroconversion of coal and bitumen mixture. Increase in toluene concentration from 15 to 50 wt% had no positive effect on the product yields.

Keywords: Hydropyrolysis; Calcium oxide; Toluene; Coal; Residue

1. Introduction

Simultaneous upgrading of coal and petroleum residue has attracted a great interest for a long time [1] over direct liquefaction of coal or upgrading of petroleum residue. In a more recent work [2] from our laboratory, upgrading of a mixture of lignite and bitumen was carried out by fast-copyrolysis at temperatures between 700°C and 1000°C with no hydrogen.

Pyrolysis reactions of fossil fuels are well known to be very complex in nature due to its retrogressive reactions [3]. Thus it becomes more complicated when in an upgrading process two hydrogen-deficient feed stocks are combined. Under these conditions use of more expensive catalysts is not economically viable. In the present work an attempt has been made to study calcium oxide as an alternate catalyst in order to simultaneously upgrade the feed stocks and improve the product quality. Limestone has been in use for long time as a trapping agent for sulfur. Several studies have established that CaO having high surface area catalyzes oxidation, gasification or combustion of low rank coal chars [4,5].

Copyrolysis is a complex system due to different nature of feed stocks present. Coal is a solid with H/C ratio less than 1 and aromatic in nature, on the other hand petroleum residue is a heavy liquid with H/C ratio more than 1 and highly rich in aliphatic components. These differences in their chemical structures

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make the residue difficult to act as a good solvent to promote upgrading process. Thus toluene was added to enhance mass transfer of hydrogen due to solvent effect under hydropyrolysis conditions. Hydrogen transferring ability of toluene through intermediate highly stable benzyl radical or benzyl cation [6] is known to be effective in stabilizing those radicals that led to the formation of high molecular weight species such as toluene-insoluble material.

In classical coprocessing technology high hydrogen pressure and long residence time are used to convert the feed stocks into distillable oil. The main objective of the present work is to lower the severity of the upgrading conditions, explore the possibility of using easily available and economical calcium oxide as an alternate upgrading catalyst and removing sulfur from the liquid or gaseous products. Another objective is to study the impact of toluene as hydrogen transferring vehicle during hydropyrolysis on the conversion and product distribution.

2. Experimental

Hydropyrolysis reactions were conducted in a vertically shaking 50 ml autoclave in a hot fluidized bed sand bath. Usually about 5 g of feed was charged into the reactor. Feed consists of 40 wt% dry ash free (daf) Alberta subbituminous coal and Athabasca bitumen as heavy residue. Most of the experiments were done with powdered calcium oxide as catalyst and a few for comparison with powdered Fe_2O_3 and $NiMo/Al_2O_3$ catalysts. A known amount of the catalyst was added to the feed and manually well dispersed before charging to the reactor. Test runs were conducted at 500–550°C and 1–10 MPa hydrogen pressure. Reactor was heated within 3 min to the required temperature and then cooled down rapidly (within 2 min) after the required residence time at the maximum temperature. The gaseous product was vented and collected in a bag and analyzed for the total hydrocarbons. A part of the residue was analyzed by simulated distillation GC method to determine total distillable oil present. Other part was extracted with THF by Soxhlet extraction and the amount of THF-insolubles was determined and hence THF-solubles was calculated.

Experimentally it was found that more than 99 wt% toluene was not converted under the reaction conditions. Only small amount of bibenzyl was obtained as product. Thus when toluene was used instead of catalyst, the amount of toluene added was subtracted from the total liquid obtained and thus the distillable oil yield was determined. In this case vacuum distillation of the product was done to determine the total liquid product. Residue was extracted by THF as before.

Results shown here are the gas yield composed of C_1 to C_4 hydrocarbons, oil yield as total distillable oil below 523°C, THF-solubles yield as the material above 523°C and THF-insolubles is the solid residue in the product. THF-insolubles was mostly unreacted coal and coke formation from heavy residue. Pitch is defined here as the nondistillable material above 523°C. All results were calculated on dry ash free basis.

3. Results and discussion

3.1. Effect of calcium oxide catalyst

Results of the preliminary test runs with powdered calcium oxide are shown in Figs. 1 and 2. They were

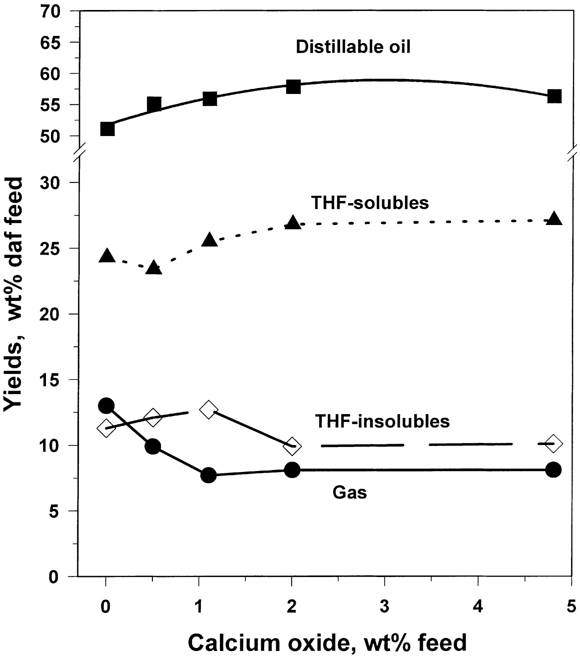

Fig. 1. Influence of calcium oxide catalyst concentration on yields. Reaction conditions: 512°C, 1 min and 3.4 MPa.

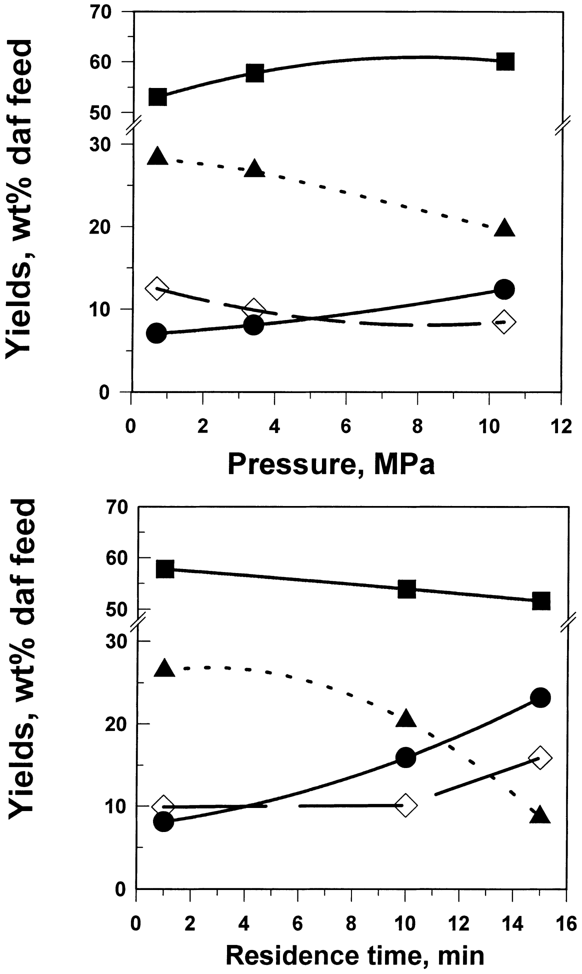

Fig. 2. Variation of yields with pressure (at 512°C and 1 min)/ residence time (at 3.4 MPa and 512°C) in the presence of 2% calcium oxide as catalyst: (●) gas, (■) distillable oil <523°C, (▲) THF-solubles, and (◇) THF-insolubles

conducted to determine standard conditions using calcium oxide as catalyst. Results in Fig. 1 show that there was an increase in the distillable oil yield by 4 wt% and decrease in the gas yield by the same amount with the addition of even 0.5 wt% CaO to the feed. Thus it is clear that in the presence of CaO hydrocarbon gaseous products had been converted into liquid products. There was slight increase in the THF-insolubles and decrease in the THF-solubles and increase in pitch conversion as discussed later on. It is difficult to distinguish only coal conversion from pitch conversion as they could overlap each other during cohydropyrolysis reaction. Thus further discussions are limited to pitch conversion only.

Distillable oil yield increases from 52 to 58 wt% with the increase in the amount of CaO from 0 to 2 wt%. Further increase in CaO had no effect on the various product yields. Therefore all other experiments were carried out with 2 wt% CaO in the feed.

Results of the preliminary studies at various residence times and pressures are shown in Fig. 2. Increase in residence time from 1 to 10 min decreased distillable oil yield from 58 to 51 wt% while increased the gas production from 8 to 22 wt%. THF-insolubles yield was not significantly influenced by ten fold increase in residence time, whereas THF-solubles decreased slightly. Thus the maximum level of conversion of pitch was essentially completed in less than 1 min. Increase in hydrogen pressure up to 10.2 MPa did not influence significantly the pitch conversion (described later on). The results clearly showed that neither higher residence time nor higher pressure have any beneficial effect on yields of products. Further results reported here are at the lowest residence time of 1 min and pressure of 3.4 MPa. A minimum pressure was used to introduce hydrogen into the reaction system.

A test run was conducted to investigate the influence of the surface area of CaO catalyst on the product distribution at 512°C, 1 min and 3.4 MPa hydrogen pressure. Calcium oxide was used in the form of 3 mm diameter pellets and below 100 mesh powder. The results in Fig. 3 clearly indicate the advantage of powdered catalyst, which produced more oil and less gas. THF-solubles increased while THF-insolubles decreased in the presence of powdered catalyst. Overall pitch conversion increased by 3 wt% when powdered catalyst was used.

3.2. *Influence of various catalysts: CaO, iron oxide and NiMo/Al_2O_3*

Fig. 4 shows the results of the hydropyrolysis of coal and heavy residue in the presence of various catalysts: calcium oxide, iron oxide and NiMo/Al_2O_3 at a loading of 2 wt% of the slurry feed. Hydropyrolysis was carried out at a hydrogen pressure of 3.4 MPa, residence time of 1 min and temperature range between 500°C and 540°C.

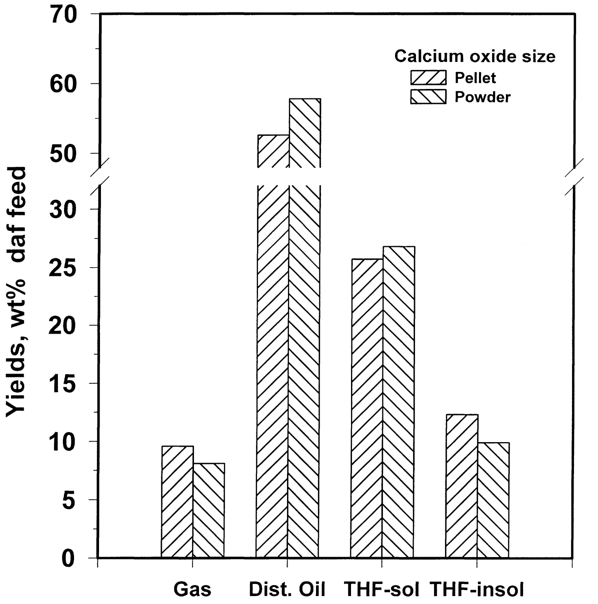

Fig. 3. Effect of calcium oxide particle size on yields. Hydropyrolysis was done with 2 wt% CaO of pellet size 3 mm diameter and powder less than 100 mesh at 512°C, 1 min and 3.4 MPa.

In all cases gas yield increased with the increase in temperature. Gas yield was almost the same (7 wt%) with all three catalysts at 512°C. With further increase in temperature up to 535°C, gas yield increased to 17 wt% with CaO compared to 12 wt% with Fe_2O_3. In case of $NiMo/Al_2O_3$ catalyst increase in gas yield was minimum. Although it is not clear why gas yield increased in the presence of CaO, it is well known [5] that gasification reactions are catalyzed in the presence of well-dispersed CaO.

Maximum distillable oil yield was about 55 wt% at 512°C and it decreased with further increase in temperature with both CaO and Fe_2O_3 catalysts, unlike in case of $NiMo/Al_2O_3$ catalyst the oil yield remained almost constant at 65 wt% above 512°C. There was a significant difference in the gas yields between CaO and Fe_2O_3 catalysts above 512°C but significant difference was not observed in their oil yields.

Fig. 4 shows a noticeable difference in the trend of THF-solubles with temperatures between CaO and Fe_2O_3 catalysts. THF-solubles decreased from 500°C to 525°C with Fe_2O_3 catalyst, but it increased with CaO. As THF-solubles is mostly derived from bitumen which contains sulfur, the reactivity of sulfur with calcium and iron could be different and thus the trend of THF-solubles yield was different. Mastral et al. [7] analyzed the tar from the hydropyrolysis of coal and reported that the characteristic of the tar changed with the severity of conditions. THF-insolubles yield also showed a different trend between CaO and Fe_2O_3 in the feed.

Complexity of the reaction mechanism that contributes to pitch conversion as described by Moritomi et al. [8] suggested that the pyridine-insoluble fraction in coal liquefaction products would consist of unreacted coal, inherently inert component of coal, semicoke from reaction and other reactive fragments, the composition of which depends on the coal, solvent type and reaction conditions. Unreacted coal and reactive fragments are suitable for conversion into soluble liquid fractions under hydrogenation conditions. Fig. 5 shows the variation of pitch conversion with temperatures in the presence of various catalysts. Pitch conversion was calculated as follows:

$$\text{Pitch conversion} = (\text{pitch in feed} - \text{pitch in product}) / \text{pitch in feed} \times 100,$$

where pitch is +523°C daf material in the feed.

In all cases pitch conversion increased significantly from 500°C to 512°C and thereafter it increased slightly with further increase in temperature. As expected, pitch conversion was much higher (68 wt% at 520°C) in the presence of $NiMo/Al_2O_3$ than other two catalysts (58 wt%). Pitch conversion was consistently slightly higher in the presence of CaO than iron oxide and was higher than that with no catalyst (50 wt%).

Reaction mechanism of the hydropyrolysis of coal and bitumen mixture with calcium oxide is not clear yet and further detailed kinetic studies are necessary to verify it. Primary goal of this paper was to evaluate the hypothesis that calcium oxide would enhance the pitch conversion reaction and distillable oil yield. A clear advantage of using CaO as catalyst was demonstrated in hydropyrolysis reaction and the catalytic activity of CaO was similar to that of iron oxide.

3.3. *Influence of toluene as additive*

In another study hydropyrolysis was carried out with the addition of toluene to the feed with no catalyst. Hydropyrolysis results are shown in Fig. 6

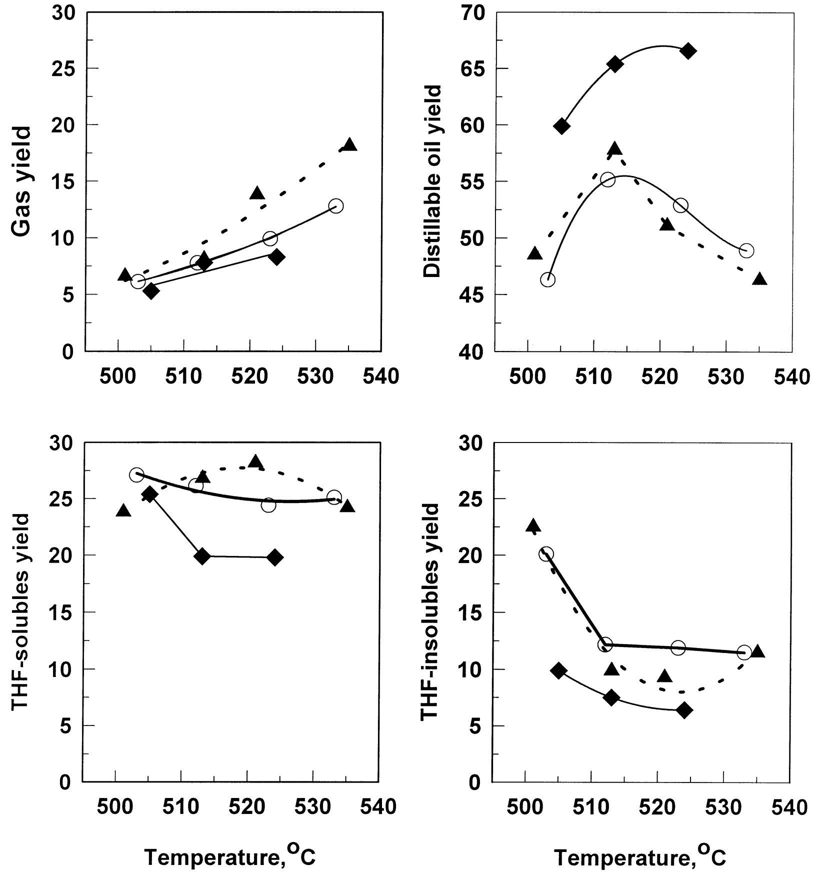

Fig. 4. Variation of different yields with temperatures using various catalysts (2 wt%) at 3.4 MPa and 1 min. Yields are in wt% daf feed. Catalyst type: (▲) calcium oxide, (○) iron oxide, and (◆) Ni–Mo/Al_2O_3.

at 512°C, 1 min and 3.4 MPa with two different toluene concentrations of 15 and 50 wt% and with no toluene. There was a significant increase in distillable oil yield from 52 wt% with no toluene to 67 wt% with 15 wt% toluene. Oil yield in the presence of 15% toluene was even higher than that obtained with other catalysts, e.g. 55 wt% obtained with CaO/Fe_2O_3 and 65 wt% with NiMo/Al_2O_3.

Yields of THF-solubles and THF-insolubles were decreased by the addition of 15 wt% toluene. Results in Fig. 5 show that pitch conversion was more than 70 wt% in the presence of toluene compared to 65 wt% with NiMo/Al_2O_3 and 55 wt% with CaO/iron oxide. Thus this is a strong indication of the hydrogen transferring ability of toluene from molecular hydrogen into the hydrocarbons fragments.

Increase in toluene concentration from 15 to 50 wt% (Fig. 6) decreased oil and gas yields, whereas increased THF-solubles and insolubles. With 50 wt% toluene in the feed there was no beneficial effect on the product distribution and thus further results reported here are at 15 wt% toluene loading only.

Fig. 7 represents the results of the product distribution under various temperatures, pressures and residence times in the presence of 15 wt% toluene. Distillable oil yield increased by about 5 wt% when temperature was increased from 503°C to 512°C or pressure was increased from 0.7 to 3.4 MPa. With further increase in temperature or pressure there was virtually no effect on the oil yields. There was almost no influence of increase in residence time from 1 to 10 min on the yields, because maximum conversion of

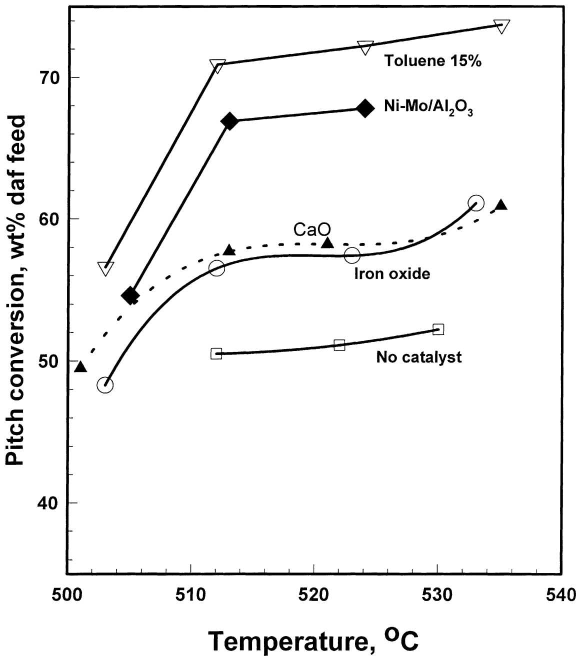

Fig. 5. Variation of pitch conversion with temperatures in the presence of various catalysts (2 wt%) and toluene (15 wt%). Reaction conditions: 1 min and 3.4 MPa.

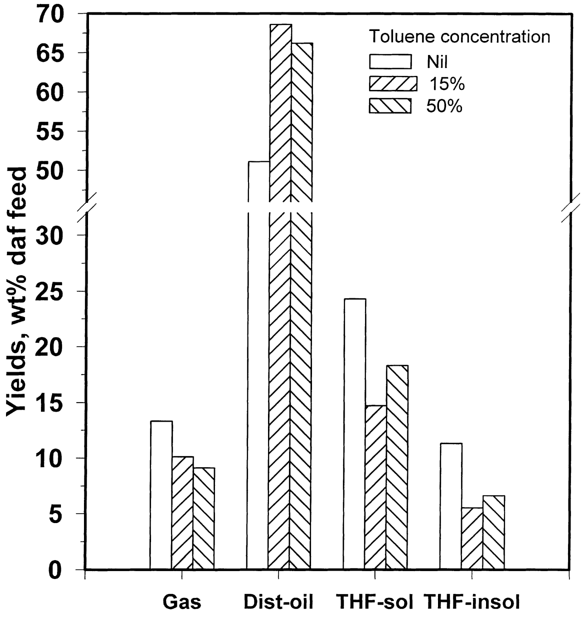

Fig. 6. Effect of toluene concentration on yields. Reaction conditions: 512°C, 1 min and 3.4 MPa.

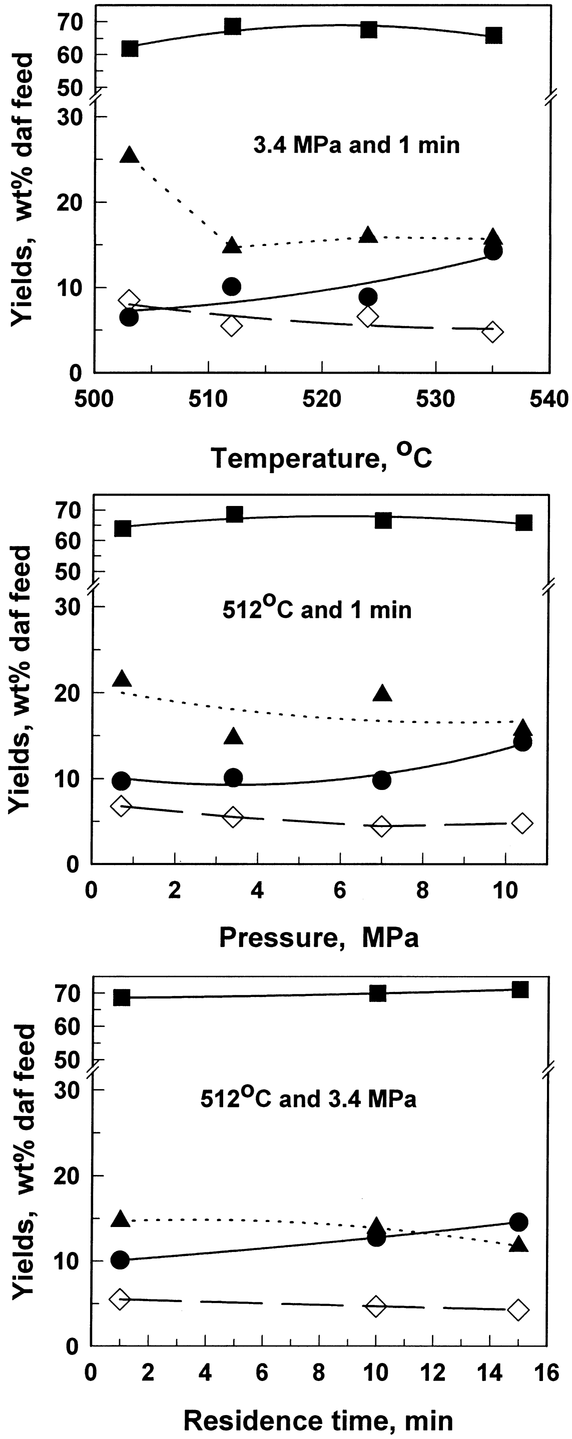

Fig. 7. Variation of yields with various reaction conditions in the presence of 15% toluene: (●) gas, (■) distillable oil <523°C, (▲) THF-solubles, and (◇) THF-insolubles.

feed was essentially achieved in less than a minute and the degree of conversion remains constant there after. In contrast to toluene additive, when solid catalysts such as CaO and Fe_2O_3 were used, hydrogen efficiency decreased above 512°C, as we observed increase in C_1 to C_4 gas formation and decrease in oil production although there was no additional THF-insolubles yield.

Above results showed that hydrogen shuttling ability of toluene was more effective at less severe conditions of shorter residence time and lower pressure at 510°C. Further increase in reaction severity neither improved nor decreased the conversion of feed into more valuable liquid product. Higher reactivity of toluene at milder reaction conditions may be due to the fact that toluene was in sub-super critical conditions (T_c=320.8°C and P_c=4.2 MPa) and hence the solvating ability was enhanced or mass transfer was increased. Another reason may be that demand of hydrogen is greatest at the initial stage of the reaction to cap thermally produced free radicals. Okuma et al. [9] also observed that hydrogen-donor solvent recovered from the hydrogenation section was more effective at milder conditions for brown coal liquefaction due to the fact that hydrogen transferring ability plays an important role at that conditions. Ramdoss and Tarrer [10] found that in case of coprocessing the total conversion increased with the increase in aromaticity and volatility of the solvent, which further confirms the fact that toluene being high aromatic and high volatile solvent had increased the conversion. Thus it could be concluded that toluene was highly effective in hydrogenation reactions with the formation of higher distillable oil yield or pitch conversion.

4. Conclusion

The present study clearly demonstrated the ability of the hydropyrolysis process for simultaneous upgrading of coal and heavy residue. Calcium oxide was found to be equally effective as iron oxide in the reaction and is a potential candidate as a catalyst for future utilization.

Both pitch conversion and distillable oil yield were more than 10 wt% higher in the presence of toluene compared to no toluene or CaO/Fe_2O_3 catalysts. It was also observed that increasing the amount of toluene did not increase the distillable oil yield. Hydrogen transferring ability of toluene was as effective as that of NiMo/Al_2O_3 catalyst in terms of oil production or pitch conversion.

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