

PYROLYSIS AND LIQUEFACTION OF ACETONE AND MIXED ACETONE/TETRALIN SWELLED MUKAH BALINGIAN MALAYSIAN SUB-BITUMINOUS COAL – THE EFFECT ON COAL CONVERSION AND OIL YIELD

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Abstract

The effect of swelling on Mukah Balingian (MB) Malaysian sub-bituminous coal macrostructure was observed by pyrolysing the swelled coal via thermogravimetry under nitrogen at ambient pressure. The DTG curves of the pyrolysed swelled coal samples show the presence of evolution peaks at temperature ranging from 235 – 295 °C that are due to releasing of light molecular weight hydrocarbons. These peaks, however, were not present in the untreated coal, indicating some changes in the coal macrostructure has occurred in the swelled coal samples. The global pyrolysis kinetics for coal that follows the first-order decomposition reaction was used to evaluate the activation energy of the pyrolysed untreated and swelled coal samples. The results thus far have shown that the activation energy for the acetone and mixed acetone/tetralin-swelled coal samples exhibit lower values than untreated coal, indicating less energy is required during the pyrolysis process due to the weakening of the coal-coal macromolecular interaction network. Moreover, liquefaction on the swelled coal samples that was carried out at temperatures ranging from 360 to 450 °C at 4 MPa of nitrogen pressure showed the enhancement of the coal conversion and oil yield at temperature of 420 °C, with retrogressive reaction started to dominate at higher temperature as indicated by decreased and increased in oil yield and high molecular weight pre-asphaltene, respectively. These observations suggest that the solvent swelling pre-treatment using acetone and mixed acetone/tetralin can improve the coal conversion and oil yields at less severe liquefaction condition.

Introduction

Coal liquefaction is usually carried out at temperatures higher than 400 °C and at relatively high pressure. Many attempts have been made to develop methods of dissolving coal at less severe conditions in order to increase coal liquefaction efficiency [1-4] and to reduce capital and operation costs [5]. It is known that, by lowering reaction severity, coal conversion reaction rates and liquid product yields will also be reduced, unless the intrinsic coal reactivity can be sufficiently enhanced [4]. Joseph [1] reported that pre-swelled US bituminous and lower rank coals (i.e. sub-bituminous and lignite) with tetrabutylammonium hydroxide, tetrahydrofuran and methanol prior to liquefaction at 400 °C and at 7.6 MPa enhanced coal conversion and product quality. He found that the enhancement depends on the coal rank and the type of swelling agent being used and suggested that the beneficial effect of swelling might be due to the expansion of the coal macromolecular structure, making it more accessible to the hydrogen donor solvent during liquefaction. In another work, Simsek [2] studied the effect of pre-swelling with various organic solvents and acid-demineralised (pre-treatment) Turkish coals on the supercritical toluene extract yield at 350 °C and at 7 MPa. They found that the highest improved liquid yields for each coal was obtained by the combined effects of pre-treatment and pre-swelling of coals. Although the combination effects proved to increase liquid yields, no simple trend between reactivity improvements with properties of the coals was observed.

In our study [6], we carried out the solvent swelling pre-treatment using hydrogen and non-hydrogen-bonding solvents on low-rank Malaysian coal. The pyrolysis of the untreated and swelled coal using thermogravimetric analyzer (TGA) under nitrogen atmosphere thus far has shown that the activation energy barrier in the swelled coals was lower with an increase in the volatile yield in comparison to the untreated sample. Moreover, the results of the treated samples also show the increase of coal reactivity as revealed by DTG results. Thus, these

preliminary results might provide useful information for coal extraction and liquefaction processes. Hence, this study investigates the effect of acetone and mixed acetone/tetralin-swelled, respectively on the pyrolysis behaviours using TGA and the conversion and product yields from the liquefaction using 1-liter high-pressure high-temperature batch-wise reactor system with tetralin as the hydrogen-donor solvent.

Materials And Methods

Coal Preparation

The sample used in this study is Mukah Balingian (MB) originating from Sarawak, Malaysia. The procedure for coal preparation has been reported earlier [7]. Table 1 represents the ultimate, proximate and petrography analyses of the untreated MB coal sample.

Solvent Swelling Procedure

The volumetric method described by Onal and Akol [8] was adopted in the measurement of swelling ratio without density correction. Acetone (analytical grade solvent from Fisher Chemicals) is used as swelling solvent. For the mixed solvent, which consists of acetone and tetralin, the volume mixed ratio was 80:20. The swelling ratio of the coal samples was measured at room temperature (30 °C) and at ambient pressure. After the swelling procedure, the swelled coal was filtered, dried in vacuum-oven at 80 °C for overnight and finally stored in bottle prior to liquefaction experiments. The determination of activation energy and volatile yield of the coal samples have been reported earlier [6]. The results of swelling ratio, activation energy and pyrolysis volatile yields of the coal samples are given in Table 2.

Coal Liquefaction Experiments

All liquefaction experiments were carried out in a 1-liter magnetically stirred (at 500 rpm) high-pressure high-temperature batch-wise reactor (Parr, 4571 model) fitted with stainless steel tubing condenser cooled with ice to ensure maximum capture of the volatile materials. The procedure of coal liquefaction has been reported earlier [7]. Briefly, 20 g of untreated or acetone-swelled coal and 200 g of tetralin were mixed in the reactor and the liquefaction was carried out at temperature ranging from 360 – 450 °C and at 4 MPa nitrogen pressure. However, for mixed acetone/tetralin coal sample, the reaction temperature used was at 420 °C. After reaching at the particular temperature, the reaction was held for 30 minutes before the system was cooled to ambient temperature. Coal conversion and the product yields of all the samples were finally evaluated [7] and are shown in Table 3.

Sample Analyses

The procedure of ultimate and proximate analyses has been reported earlier [7]. The ultimate analyses were carried out using Elemental Analyser Leco 932 model. The proximate analyses were done using Thermogravimetric analyzer DTA/DSC TA model SDTQ600 under nitrogen gas atmosphere with heating condition follows the ASTM D2974 [9].

Table 1: Characteristics of MB coal sample.

Ultimate analysis	(wt% daf)	Proximate analysis	(wt% db)
Carbon	63.9	Volatile matter	44.7
Hydrogen	5.1	Fixed Carbon	51.1
Nitrogen	1.9	Ash content	4.2
Sulphur	0.5		
Oxygen*	28.6		

Calorific Value = 24.60 MJ/kg

*Calculated by difference.

Table 2: Results of swelling ratio (Q), activation energy (E_i, kJ/mol) and pyrolysis volatile yield (VY) of MB coal.

Sample	Q	E _i	VY(%)
Untreated	1.0	312.2	37.6
Tet-sw	1.0	246.3	41.4
Ace-sw	1.3	230.5	40.4
Ace+Tet-sw	1.4	131.6	49.8

Tet-sw Tetralin-swelled

Ace-sw – Acetone-swelled

Ace+Tet-sw – Acetone/Tetralin-swelled

Results And Discussion

Effect of Swelling On Coal by Pure and Mixed Solvents During Pyrolysis

Table 2 shows the results of swelling ratio, activation energy and volatile yield of untreated, acetone-swelled and mixed acetone/tetralin-swelled of MB coal samples. From the table, it can be seen that the swelling ratios of the coal in acetone and mixed acetone/tetralin are higher than that of tetralin. This observation indicates the interaction of nucleophile in the H-bonding solvent (i.e. acetone) with the reactive sites such as hydroxyl, carboxyl and carbonyl that are presence in the coal forming hydrogen bondings. The increase in solvent-coal interactions enhanced the bonds strength, thus weakened the coal-coal macromolecular interactions, and promotes the swelling process of the coal. Tetralin, which is a non-H-bonding solvent, however, did not exhibit any swelling activity with the swelling ratio value closed to that of untreated coal [6]. Interestingly, when tetralin was mixed with acetone, the swelling ratio of the coal increased to a value of 1.4, which is slightly higher than the pure acetone. This minor increment indicates an additional interaction occurred between the coal macromolecular network and the solvents mixture. The effect of swelling by the mixed solvents seem to weakens the coal macromolecular network rigidity and promotes the diffusion of the solvent mixtures, though the exact mechanism is still not well understood. Further, in order to prove this effect, the solvent pre-swelled and untreated coal samples were subjected to pyrolysis via thermogravimetric analysis and the activation energy of the process was evaluated. The global pyrolysis kinetics for coal that follows the first-order decomposition reaction was used to determine the activation energy of the process [10]. Indeed, the mixed solvent swelled coal exhibits the lowest activation energy with an increased in volatile yield, indicating less energy was required during the pyrolysis process due to the weakening of the coal-coal macromolecular interaction network that occurred during swelling process. Thus, this observation indicates the presence of synergistic effect of the mixed solvent towards swelling activity of the coal that enhanced the lowering of the activation energy with an increased in volatile yield during pyrolysis.

Figure 1 shows the DTG curves of untreated, acetone-swelled and mixed acetone/tetralin-swelled coal during pyrolysis. Apparently, both the pyrolysed acetone and mixed acetone/tetralin-swelled coal samples show the presence of evolution peaks at temperatures ranging from 175 to 395 °C that are due to the releasing of the light molecular weight hydrocarbons [10]. These peaks however, were absence in the untreated coal. Another point of interest is that for the mixed acetone/tetralin-swelled coal sample there appears to be another evolution peaks at high temperature ranging from 500 to 650 °C that are due to the released of heavy hydrocarbons [10], and were not presence apparently in both untreated and acetone pre-swelled coal samples. Hence, these observations further proves that some changes in the coal macrostructure have occurred especially in the mixed solvents swelled coal sample that promotes the released of light and heavy molecular weight hydrocarbons during pyrolysis. Hence, this shows that the swelling pre-treatment on coal would possibly increase the liquefaction performance by increasing coal conversion and product yields (especially percent oil) at less severe conditions.

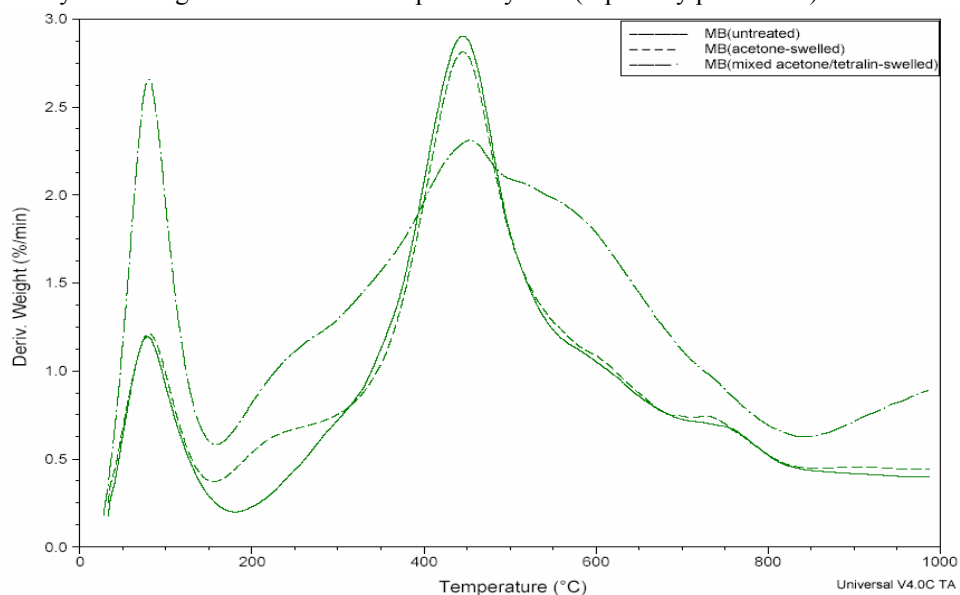


Figure 1: The DTG curves of untreated, acetone-swelled and mixed acetone/tetralin-swelled of MB coal samples.

Effect of Swelling on Coal Conversion and Oil Yield

Table 3 shows the percent of coal conversion and product yields of liquefaction on the untreated, acetone-swelled and mixed acetone/tetralin-swelled coal samples.

Table 3: Liquefaction results of untreated, acetone- and mixed acetone/tetralin-swelled coal.

Temp. °C	% Coal conversion			Products Yield								
				% Oil + Gas			% Asphaltene			% Preasphaltene		
	Unt.	Ace.	Mix.	Unt.	Ace.	Mix.	Unt.	Ace.	Mix.	Unt.	Ace.	Mix.
360	42	35	-	28	24	-	8	5	-	6	6	-
380	57	43	-	44	29	-	8	3	-	5	11	-
400	66	62	-	50	46	-	10	6	-	6	10	-
420	84	86	86	67	70	78	8	6	1	7	10	7
450	90	83	-	80	75	-		4	-	2	4	-

Unt. = Untreated; Ace. = Acetone-swelled; Mix. = Mixed acetone/tetralin-swelled.

Liquefaction conditions: 4 MPa, 1:10 coal:solvent, 30 min reaction time and stirred at 500rpm.

Apparently, the results thus far showed that the percent of coal conversion and oil yield obtained during liquefaction of acetone-swelled coal was lower than the untreated coal with preasphaltene predominantly increased at temperature below 400 °C. The fact that as the liquefaction temperature increased at above 350 °C, the coal starts to soften and eventually undergo fragmentation forming preasphaltene and asphaltene [7]. However, with the swelled coal sample, much smaller molecules are being formed due to the weakening of the coal-coal macromolecular interaction as revealed by the DTG curves. The hydrogen donor solvent should cap these smaller radical molecules rapidly in order to prevent repolymerisation reaction. The fact that high formation of preasphaltene suggests that repolymerisation reaction starts to dominate due to the inability of the donor solvent to cap these smaller molecules at temperature below 400 °C. However, as the liquefaction temperature increased beyond 400 °C, a high amount of coal conversion and oil yield being obtained with decreased amount of preasphaltene formation.

Obviously, the effect of mixed solvent swelled coal during liquefaction can be seen by the high percent of oil yield of 78 % at 420 °C, that is higher than that achieved in the acetone- swelled and untreated coal samples. The increase in oil yield corresponds to the decrease in asphaltene and preasphaltene. These observations seem to agree with the pyrolysis which resulting in the lowest activation energy with the greater increased of volatile yield that indicate the high reactivity of the mixed acetone/tetralin-swelled coal. Thus, these phenomenons proved the beneficial effect of mixed solvent-swelled coal in enhancing coal conversion and oil yield prior to liquefaction.

Conclusion

The effect of acetone and mixed acetone/tetralin-swelled on the coal pyrolysis using TGA and the liquefaction products using 1-liter high-pressure high-temperature batch-wise reactor system with tetralin as the hydrogen-donor solvent were studied. The results thus far have shown that the activation energy for the acetone and mixed acetone/tetralin-swelled coal samples exhibit lower values than the untreated coal, indicating less energy is required during the pyrolysis process due to the weakening of the coal-coal macromolecular interaction network. Moreover, liquefaction on the swelled coal samples showed the enhancement of the coal conversion and oil yield at temperature of 420 °C, where the oil yield was greatly increased for mixed acetone/tetralin-swelled with further decreased in asphaltene and preasphaltene, respectively. Thus, these observations proved the beneficial effect of swelling pre-treatment on liquefaction at less severe condition.

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