

# Direct liquefaction on low rank Batu Arang coals of Malaysia: Influence of petrographic composition

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**Abstract:** A direct liquefaction study was performed on a set of low-rank Malaysian coals from Batu Arang, Selangor in Peninsular Malaysia. The analysis was carried out in a 1000 mL high temperature and high-pressure reactor batch-wise system using tetralin as hydrogen donor solvent, at temperature of 420°C and at pressure of 4MPa. The influence of maceral composition was investigated based on comparison made on the percentage of coal conversion and product yield for the three coals that were analysed. These analysed samples contain reactive macerals (vitrinite + exinite) in the range of 76% - 92%. The high coal conversion and oil+gas yields are attributed predominantly to the high content of reactive macerals of vitrinite and exinite maceral groups, with some contribution from the inertinite maceral group. This suggests the analysed Batu Arang coals possess good potential to act as an alternative liquid fuel in the future through direct liquefaction process.

**Keywords:** coal conversion, coal liquefaction, reactive macerals, semifusinite, 'oil+gas' yields

## INTRODUCTION

The need for energy is forever growing worldwide, most demanding being within Asian countries (IEO 2010; 2013). At the current rate of consumption, the Malaysian crude oil reserve has been forecasted to last for about 25 years (Inside Malaysia, 2012). There are several options available as an alternative energy to crude oil such as biodiesel, solar and hydro energy. However, the World Energy Outlook (IEA, 1998) reveals that fossil fuels will continue to dominate the energy mix; with 95% of the additional energy demands between 1995 and 2020 will be met by fossil fuels. Coal, although commonly considered as unfriendly source of energy due to its high sulphur content, is still recognized as one of the most important source of energy for the foreseeable future. Moreover, the world's recoverable reserves of coal are approximately five times as large as the proved reserves of either oil or natural gas and that we have enough coal to last hundreds of years (Ecotricity, 2014).

Malaysia has a considerable reserves with estimate at end of 2011 stood at 1,819 Mt, of which 1,468 Mt or 80.7 % were located in Sarawak, 334 Mt or 18.3 % in Sabah, while the remaining 1 % in Peninsular Malaysia (Sia and Abdullah, 2012). Hutchison (2009) identified the Batu Arang Basin of the Peninsular Malaysia to belong to the half graben series that is part of a southward extension of the Tertiary intermontane basins of Thailand. The geology of the coal measures of Batu Arang has been discussed by previous workers such as Stauffer (1973) and more recently by Raj *et al.* (2009). Wan Hasiah and Abolins (1998) reported on the occurrence of oil shales within the Batu Arang coal measures which were shown to possess excellent oil generating potential. Thus, coals as well as oil shales can be considered as obvious alternatives to crude oil,

if they could be converted cheaply and effectively to meet the current demands of oils in various industries.

## METHODOLOGY

Direct hydrogenation of coal was developed by Bergius, and commercial plants operated in Germany, Japan and United Kingdom before and during the World War II (Durie and Smith, 1975). A description of liquefaction technologies was recently summarized by Liu *et al.* (2010). Most hydrogenation paths require that coal, dispersed in a thermally stable 'solvent' and/or 'hydrogen-donor', such as tetralin or a component separated from the product liquid, is passed into a pressurized (10 MPa or more) autothermal reactor at temperature between 400° and 500°C (Diessel, 1998). In this study three coal samples collected from an abandoned mine pit in Batu Arang, Selangor, Malaysia were subjected to liquefaction analysis by direct hydrogenation process using a batch-wise liquefaction system shown in Figure 1 as was previously described by Ishak *et al.* (2005).

## Ultimate and Proximate Analyses

Prior to the liquefaction experiment, ultimate and proximate analyses were performed on the three coal samples. An ultimate analysis was carried out using a Leco 932 model Elemental Analyzer with helium as the carrier gas. The values for carbon, hydrogen, sulfur and nitrogen were directly obtained, whilst the percentage of oxygen was determined from the difference. Each sample was analyzed in duplicate. Proximate analyses for the determination of moisture, volatile matter, fixed carbon and ash content were carried out using Thermogravimetric Analyzer DTA/DSC TA Model SDT Q600 under nitrogen gas atmosphere with heating condition according to the ASTM D2974-13. The

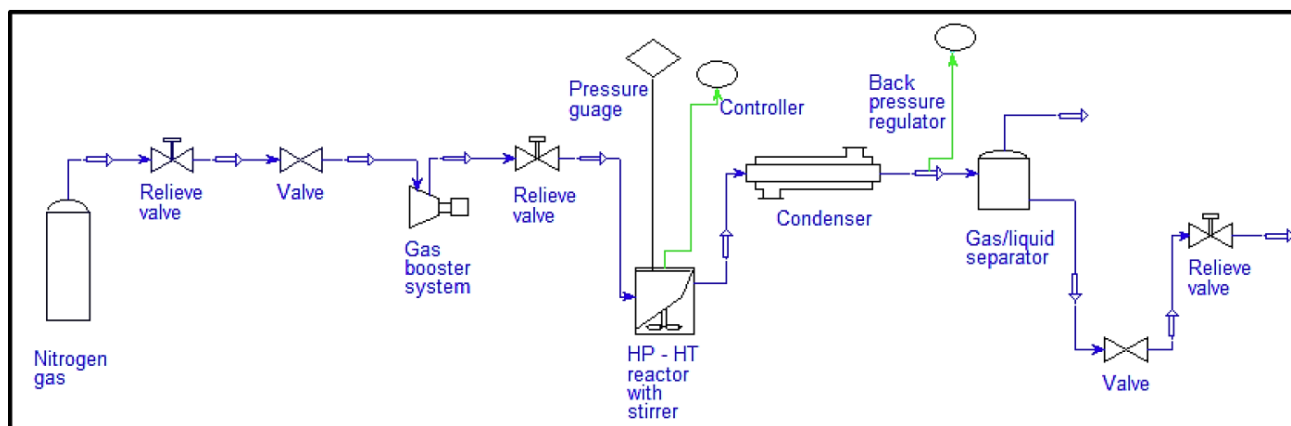


Figure 1: Experimental set-up of the batch-wise liquefaction system (adapted after Ishak *et al.*, 2005).

calorific value of the samples was carried out using Bomb calorimeter Leco AC-350 model following the ASTM D2015-96.

### Petrographic Analyses

For petrographic studies, the coal samples were crushed to approximately 2 mm in size and mounted in Serifix resin mixed with resin hardener in mounting cups. Once hardened the samples were then polished with successively finer grades of silicon carbide and finally, alumina using water as lubricant. Microscopical examination was carried out principally under reflected light, both in white light and blue light excitation for maceral analysis (of 1000 counts) using an oil immersion objective.

### Coal Liquefaction Experiments

Prior to the liquefaction analysis, the coals were subjected to the following sample preparation procedures. The coal samples were pulverized and sieved through progressively finer screen to obtain particle sizes of <212  $\mu\text{m}$ . The pulverized coals were sieved by shaking for about 30 minutes and subsequently dried in a vacuum oven at 105°C overnight. These moisture free (MF) samples were then stored in a tightly-cap bottle prior to usage.

A direct liquefaction experiment was conducted in a 1000 mL magnetically stirred (i.e. stirring at 500 rpm) high-pressure high-temperature batch-wise reactor (Parr, 4571 model) fitted with ice-cooled stainless steel tubing condenser to ensure maximum capture of the yielded volatile matter. The methodology adopted in this study is as described by previous workers (Ishak *et al.*, 2005). Tetralin was used as the hydrogen donor solvent. 20 g of coal and 200 g of tetralin (1:10 coal: solvent ratio at 22% of reactor-free volume) were mixed in the reactor and the liquefaction was carried out at temperature of 420°C and pressure of 4 MPa. A leak-check test was performed prior to starting the experiment, following which the reactor was pressurized with nitrogen and heated to reaction temperature at a rate of 5°C min<sup>-1</sup>. This reaction was held for 30 minutes. Upon completion, the reactor was then cooled and depressurized to ambient pressure. To recover

the solid and liquid materials, the reactor were thoroughly washed out and extracted with THF solvent yielding the THF insoluble materials (i.e. coal liquefaction residues) and THF-soluble. Subsequently the THF-soluble was separated into oil (hexane-soluble), asphaltene (toluene-soluble, hexane-insoluble) and preasphaltene (THF-soluble, toluene-insoluble) using Soxhlet apparatus. The coal conversion and the product yields were evaluated by equations (1) and (2) as follows:

$$\text{Coal conversion [wt.\% daf]} = \frac{W_{\text{coal}}(1 - \alpha_0) - W_{\text{residue}}(1 - \alpha)}{W_{\text{coal}}(1 - \alpha_0)} \times 100 \dots\dots (1)$$

$$\text{Product yield [wt.\% daf]} = \frac{W_i}{W_{\text{coal}}(1 - \alpha_0)} \times 100 \dots\dots (2)$$

where,  $W_{\text{coal}}$ ,  $W_{\text{residue}}$  and  $W_i$  were the weight of parent coal, coal liquefaction residue and each constituent of extracts (i.e. oil+gas, asphaltene and preasphaltene), respectively whilst  $\alpha_0$  represent ash content in the parent coal and  $\alpha$  represent the residue. Tetralin was not recovered in order not to remove some other volatile products. The yield of oil+gas products was calculated by differences i.e. subtracting the total mass of asphaltene + preasphaltene + coal liquefaction residue from the mass of original dry, ash-free (d.a.f) coal subjected to liquefaction. The calculated results are shown in Table 1.

## RESULTS AND DISCUSSION

Table 2 show the ultimate, proximate and maceral composition of the analysed Batu Arang (BAC) coal samples. The low thermal maturity of the analysed samples is as indicated by the relatively high volatile matter in the range of 44.4-45.1% db. Based on a previous study, the vitrinite reflectance values of the Tertiary Batu Arang coals were reported to be in the range of 0.37-0.42%Ro (Wan Hasiah and Abolins, 1998). The % C of the analysed samples ranges from 68.7-73.8% and % H ranges from 5.2-5.5% daf. The H/C ratio is < 1.0% (0.88-0.94%). The ash content of these coals is generally low (5.8-6.7%) thus in agreement with the low mineral matter content (<1%) as determined petrographically.

**Table 1:** Liquefaction results of Batu Arang coals.

Samples	Weight (g)						Product yields			Coal conversion (wt%,daf)
	Coal	Coal (daf)	Oil+gas	Asphaltene	Pre-asphaltene	Residue	Oil+Gas (%)	Asphaltene (wt%,daf)	Pre-asphaltene (%.daf)	
BAC1	20.32	18.33	13.67	0.46	2.41	1.80	74.54	2.51	13.15	91.16
BAC2	20.21	18.35	14.35	0.62	1.20	2.19	78.18	3.38	6.54	89.19
BAC3	20.07	18.34	14.78	0.92	1.63	1.01	80.60	5.02	8.90	94.97

**Table 2:** Ultimate, proximate and petrographic analyses of Batu Arang coals.

Samples	Ultimate analysis (wt%, daf)		Proximate analysis (wt%, db)		Petrographic analysis (vol.%)	
BAC1	Carbon	73.80	Volatile matter	44.50	Vitrinite	41
	Hydrogen	5.46	Fixed carbon	49.30	Exinite	44
	Nitrogen	1.02	Ash content	6.20	Inertinite	15
	Sulfur	0.72			Mineral matter	Trace
	Oxygen*	19.00				
	H/C ratio	0.89				
	Calorific value:	27.10MJ/kg				
BAC2	Carbon	68.69	Volatile matter	45.10	Vitrinite	34
	Hydrogen	5.36	Fixed carbon	48.22	Exinite	42
	Nitrogen	0.37	Ash content	6.68	Inertinite	23
	Sulfur	0.68			Mineral matter	Trace
	Oxygen*	24.90				
	H/C ratio	0.94				
	Calorific value:	26.90MJ/kg				
BAC3	Carbon	70.45	Volatile matter	44.38	Vitrinite	48
	Hydrogen	5.19	Fixed carbon	49.78	Exinite	44
	Nitrogen	0.33	Ash content	5.84	Inertinite	8
	Sulfur	0.64			Mineral matter	Trace
	Oxygen*	23.39				
	H/C ratio	0.88				
	Calorific value:	27.20MJ/kg				

daf=dry ash free basis. Db=dry basis. \*calculated by difference

Based on the petrographic analysis, the analysed samples contain reactive macerals (vitrinite + exinite) in the range of 76% - 92%. Although there is no significant difference, the maceral composition was slightly dominated by exinite (liptinite) maceral group in two of the samples (BAC1 & BAC2), while in the other sample (BAC3) it is dominated by vitrinite. The most dominant vitrinite maceral in these samples is desmocollinite or collodetrinite (ICCP, 1998) which is a structureless form of vitrinite maceral (Figure 2a). On the other hand, the composition of inertinite maceral group is much lower compared to the vitrinite and liptinite maceral groups whereby the lowest content is in Sample BAC3. The most dominant inertinite maceral in the analysed samples is semifusinite (Figure 2a), whilst cutinite (Figure 2b) and liptodetrinite (Figure 2a) are amongst the most common liptinitic macerals.

The liquefaction product was calculated for all of the analysed samples, and results of the product yields i.e. oil+gas, asphaltene and preasphaltene are shown in Table 1.

The conversion in the range of about 89 to 95% was obtained for the three samples. This is predominantly attributed to the reactive macerals i.e. vitrinite and exinite (liptinite). Note that all the analysed samples contain about

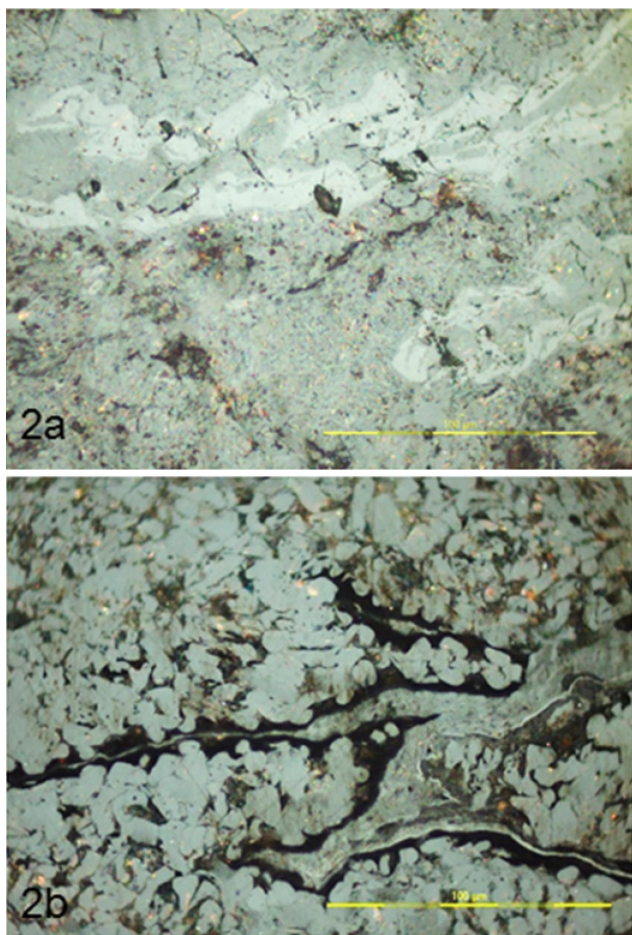
the same amount of exinite (42-44%) with the difference being in the vitrinite (34-48%) and inertinite (8-23%) content. Coals containing high proportion of vitrinite and liptinites macerals are long known as reactive macerals and have been correlated with high conversion capacity in liquefaction process (e.g. Given *et al.*, 1975) as is the case observed in this study (Figure 3). Based on the current study, the influence of the 'inert' nature of the inertinite maceral group is apparent as sample (BAC2) having the highest inertinite content recorded the lowest value of percent coal conversion (Figure 4). However, the inertinite content does not seem to have the same influence on the "oil + gas" product yield whereby BAC2 recorded an intermediate value amongst the analysed samples (Figure 5). This may suggest certain inertinite maceral(s) of particularly low rank coals may not be 100% inert and is possibly partially reactive. In support, earlier workers such as Heng and Shibaoka (1982) who analysed oil yield from Australian inertinite, reported that it yielded approximately three quarters that of the vitrinite from the same feed coal. A more recent study by Wang *et al.* (2010) reported that semifusite-rich coals recorded a reasonably high conversion and "oil + gas" yields, thus indicative of the reactive nature of certain inertinite macerals.

**CONCLUSION**

The high coal conversion (89% - 95%) of the studied Batu Arang coals correlated well with the high content of reactive macerals i.e. vitrinite and exinite (76% - 92%) in particular structureless vitrinite, cutinite and liptodetrinite. In this study, inertinite maceral, in particular semifusinite has also been identified to be partially reactive. This assumption is made based on the high 'oil+gas' yields in the sample containing reasonably high inertinite content, and this could be attributed to the low rank nature of these coals. These Batu Arang coals, or coals of similar petrographic properties may therefore be considered as a potential alternative energy resource for liquid fuel in the future.

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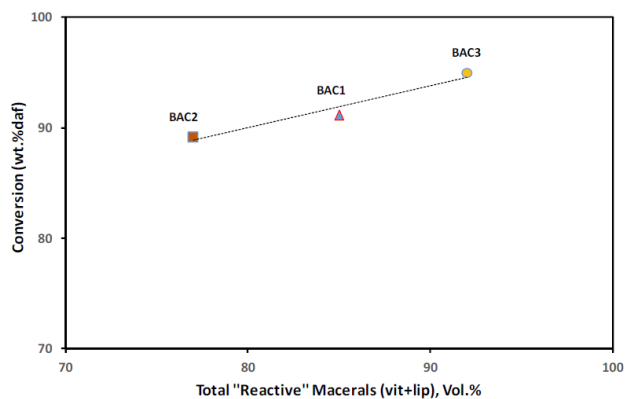
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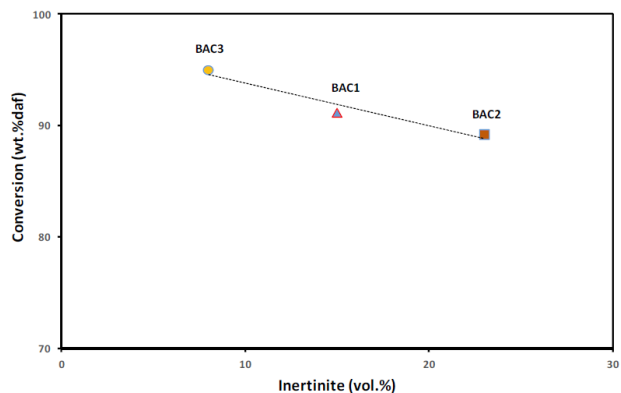
**Figure 2:** 2a, Structureless vitrinite (desmocollinite) forming groundmass of the Batu Arang coal and with common occurrence of high reflecting semifusinite maceral as observed under reflected white light. 2b, Low reflecting structured cutinite maceral associated with structureless vitrinite matrix in the analysed Batu Arang coal as observed under reflected white light. Scale bar 100 µm.

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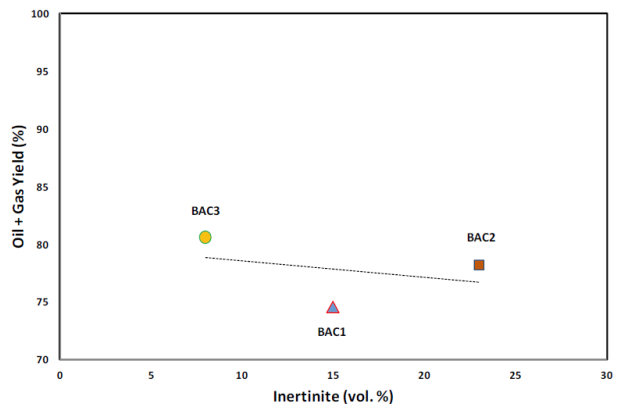
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**Figure 3:** Relationship between coal conversion and reactive maceral concentration for the analysed coal samples.



**Figure 4:** Relationship between conversion and inert component in the analysed coal samples.



**Figure 5:** Relationship between oil + gas yield and inert component in the analysed coal samples.

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