

## Nano Transition Metal Sulfide Catalyst for Solvolysis Liquefaction of Soda Lignin

(Pemangkin Sulfida Logam Peralihan Bersaiz-Nano untuk  
Pencecairan Solvolisis Soda Lignin)

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### ABSTRACT

*Solvolysis liquefaction of soda lignin in the presence of various transition metal sulfide catalysts was studied to investigate the catalyst effects on the oil and gas yields, conversion rate and higher heating value (HHV) of oil. Nanosized copper sulfide, iron sulfide and molybdenum sulfide were successfully synthesized via a simple hydrothermal method under reaction temperature 200°C for 90 min. The addition of transition metal sulfide based catalysts (CuS, MoS<sub>2</sub> and FeS<sub>2</sub>) enhanced both production of the oils and gas and the higher heating value (HHV) of oil products. A high oil and gas yields of 82.1% and 2890 cm<sup>3</sup> was obtained with MoS<sub>2</sub> at 250°C for 60 min. Elemental analyses for the oils revealed that the liquid products have much higher heating values than the crude soda lignin powder.*

*Keywords: Catalyst; higher heating value; hydrothermal; soda lignin; solvolysis liquefaction*

### ABSTRAK

*Pencecairan solvolisis soda lignin dengan kehadiran pelbagai mangkin sulfida logam peralihan telah dikaji tentang kesan mangkin ke atas hasil minyak dan gas, kadar penukaran dan nilai pembakaran tinggi (HHV) minyak solvolisis. Sulfida kuprum, sulfida ferum dan sulfida molibdenum yang bersaiz nano telah berjaya disintesis melalui kaedah hidroterma di bawah suhu 200°C dalam masa tindak balas sepanjang 90 minit. Penggunaan mangkin dalam proses solvolisis telah meningkatkan kadar hasil minyak serta gas dan produk minyak telah berjaya mencapai nilai pembakaran (HHV) yang tinggi. Hasil minyak dan gas yang tinggi iaitu: 82.1% and 2890 cm<sup>3</sup> telah diperolehi dengan penggunaan mangkin MoS<sub>2</sub> di bawah suhu 250°C selama 60 minit. Analisis unsur untuk minyak solvolisis menunjukkan produk cecair daripada pencecairan solvolisis mempunyai nilai pembakaran tinggi (HHV) yang lebih tinggi berbanding dengan serbuk soda lignin.*

*Kata kunci: Hidroterma; mangkin; nilai pembakaran tinggi; pencecairan solvolisis; soda lignin*

### INTRODUCTION

Recently, crystalline and partially crystalline nano-sulfides have been extensively studied due to their numerous potential applications as catalysts for coal liquefaction, solid lubricants, rechargeable batteries, solar cell devices, and coatings for microwave shields (Alejandra et al. 2008; Hu et al. 2002; Qin et al. 2005; Tian et al. 1996). Particles size plays an important role in determining the dispersivity and activity of the catalysts, and the optimum size ranges from 10 to 20 nm (Tian et al. 1996). Control over the size of sulfide particles is therefore of great importance. Various techniques have been developed to synthesize transition metal sulfides, including mechanochemical (Balaz et al. 2003), thermalysis (Monteiro & Trindade 2004), microwave irradiation (Liao et al. 2001) and hydrothermal processes (Zou et al. 2007). Among them, hydrothermal synthesis offers an attractive method due to its simplicity and productivity. In addition, under supercritical condition it leads to the formation of nanoscale products which cannot be obtained by classical routes (Subba et al. 2008).

Traditionally lignin has been viewed as a waste material or a low value by-product of pulping with its utilization predominantly limited to be use as a fuel to fire the pulping boilers. Indeed it has been estimated that only 1–2% of lignin is isolated from pulping liquors and used for specialty products (Lora & Glasser 2002). Besides, used as a low-grade fuel to provide heat in pulp and paper industry, the designs of ethanol production in a lignocellulosic plant also show lignin being used to provide process heat. It would be ideal to convert the lignin into a higher value fuel or chemical (Qian et al. 2007).

To date, thermochemical liquefaction has gained growing attention and is considered to be a promising method for converting biomass into higher value fuels. The advantage of this process is that it does not require feedstocks drying process. Since most biomass usually has high moisture content, a drying process requires much heating energy due to large latent heat of water vaporization. Therefore, thermochemical liquefaction can be an effective method for converting woody biomass into

oil or other types of fuels. Biomass energy conversion methods are divided into the biochemical methods (such as methane fermentation and alcoholic fermentation) and the thermochemical methods such as direct combustion, pyrolysis, gasification and liquefaction (Huber et al. 2006). From previous study, the bio-oil produced by liquefaction has a lower oxygen content and therefore higher energy content than pyrolysis-derived oils. There are a variety of liquefaction processes including hydrothermal processing (water or aqueous solvent), hydrolysis (no carrier liquid solvent), and solvolysis (reactive liquid solvent) (Qian et al. 2007).

A number of catalysts have been used for liquefaction including alkali which comes from the alkaline ash components in wood, alkaline oxides, carbonates, and bicarbonate, metals such as zinc, copper and nickel, formate, iodine, cobalt sulfide, zinc chloride, ferric hydroxide and Ni and Ru heterogeneous catalysts which aid in preferential hydrogenation (Huber et al. 2006).

In this paper we present a hydrothermal approach to synthesize transition metal (Cu, Mo, and Fe) sulfide nanoparticles in the presence of sodium thiosulfate and hydroxylamine sulfate. The analyses of the sulfide nanoparticles included studies on the crystal structure, particle size and element contents by using X-ray diffraction analysis (XRD), transmission electron microscopy (TEM), and energy dispersive X-ray analysis (EDX). We also investigate the effect of these transition metal sulfide catalysts on yield of oil, gas, conversion and HHV (higher heating value) for solvolytic oils.

## EXPERIMENTAL DETAILS

### CATALYST PREPARATION

For sulfidation of copper, a solution of sodium thiosulfate-5-hydrate, hydroxylamine sulfate and cupric sulfate-5-hydrate in ratio of 3:2:1, was mixed with 60 mL of distilled water and the mixture was heated to 200°C in a stainless steel autoclave under stirring for 90 min and cooled to room temperature. Nitrogen gas was purged into the autoclave before the reaction. Hydrothermal synthesis of molybdenum sulfide and iron sulfide nanoparticles were carried out by a similar synthetic procedure, which sodium molybdate and ferrous chloride-4-hydrate were used, respectively as the precursor material. The formed precipitate was filtered off, washed and centrifuged with distilled water and methanol for several times and then oven-dried at temperature 80°C for 24 h.

X-ray diffraction (XRD) analyses were carried out using an X-ray diffractometer (Siemens D5000) and Cu  $K_{\alpha}$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). The powders were continuously scanned at a scanning rate of  $0.02^{\circ} \text{ s}^{-1}$  using a  $2\theta$  range of 20-80°. A transmission electron microscopy (TEM, Philips CM12) was employed to examine the size and dispersivity of the particles. The average particle size was measured from at least 50 particles from the TEM micrographs and the standard deviation was calculated. The elemental

compositions of the synthesized products were examined using an energy dispersive X-ray (EDX) spectroscopy, respectively.

### SOLVOLYSIS LIQUEFACTION

The experiment was carried out in a 200 mL stainless-steel autoclave with a stirrer. In each test, the reactor was charged with 5 g lignin, 20 mL EG and 3 wt% of the as-synthesized CuS, FeS<sub>2</sub> or MoS<sub>2</sub> nanomaterial. The headspace inside the autoclave was purged with nitrogen gas for at least 5 min, and the initial pressure was recorded. The reactor was heated to the desired temperature (200, 250 and 300°C) and stirring was continued for a total period of 30 or 60 min. After completion, the autoclave was allowed to naturally cool down to room temperature. The products of the liquefaction include gaseous, aqueous and solid phases. The gas released from the autoclave into a water pail, which the gas were trapped by a measuring cylinder inside the water pail. The volume of gas released was recorded. The liquid product was filtered in order to separate the water soluble fraction and water-insoluble fraction. The water soluble fraction was then evaporated at 100-120°C to remove the water completely. The resulting product was denoted as water soluble part. The water-insoluble fraction was then washed and solubilized with acetone and all the acetone insoluble contents were separated by filtration. The acetone-soluble fraction was then evaporated at 70-80°C to remove the acetone completely. The resulting product was denoted as oil. The acetone-insoluble fraction on the other hand was dried at 105°C to obtain the solid residue. Figure 1 shows a flow chart of the overall process. The yield of the oil was defined as weight percentage of the raw lignin. The conversion rate and oil yield were calculated using the following formulae:

$$\text{Oil Yield (wt\%)} = \frac{\text{weight of oil}}{\text{weight of biomass}} \times 100\% \quad (1)$$

$$\text{Residue (wt\%)} = \frac{\text{weight of solid residue}}{\text{weight of biomass}} \times 100\% \quad (2)$$

$$\text{Conversion Rate} = 100\% - \text{weight of residue (wt\%)} \quad (3)$$

The C, H and N contents of the raw lignin and oil product were determined using the ThermoFinnigan Eager-300 CHNS analyzer. The oxygen content was estimated based on the assumption that the samples contain only C, H, N and O.

## RESULTS AND DISCUSSION

### CATALYST CHARACTERIZATION

*Copper sulfide* Figure 2a shows the X-ray diffraction pattern of the copper sulfide nanoparticles that were produced by mixing CuSO<sub>4</sub>·5H<sub>2</sub>O with Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O and (H<sub>3</sub>NO)<sub>2</sub>·H<sub>2</sub>SO<sub>4</sub> in the hydrothermal process. This pattern confirmed the formation of pure hexagonal covellite phase (CuS),

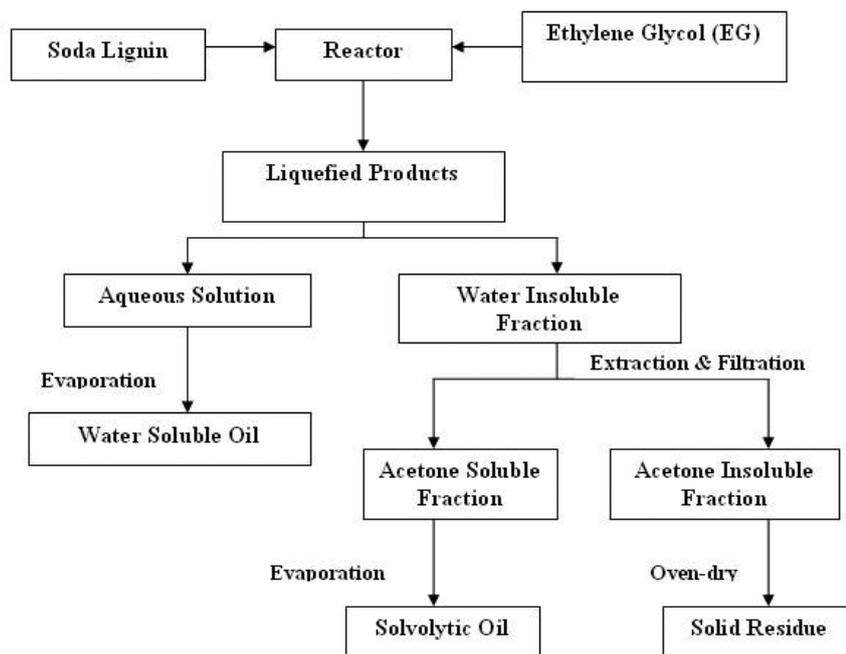


FIGURE 1. A brief scheme of the solvolysis liquefaction process and product separation

which match well with the standard XRD pattern (JCPDS Card File No. 06-0464;  $a = 3.792 \text{ \AA}$ ,  $b = 3.792 \text{ \AA}$  and  $c = 16.34 \text{ \AA}$ ). No diffraction peaks relating to  $\text{Cu}_{1.8}\text{S}$  and  $\text{Cu}_2\text{S}$  were observed, indicating the high purity of the nanoparticles. The sharp diffraction peaks revealed that well crystallized sulfide nanoparticles could be produced through the hydrothermal

process. The TEM (Figure 2b) image demonstrates the high-dispersivity of the produced CuS nanoparticles. The estimated average particle size was  $6.18 \pm 1.59 \text{ nm}$ . Compositional analysis using EDX characterization (Figure 2c) indicates that the as-synthesized particles are CuS, which agrees well with the XRD pattern.

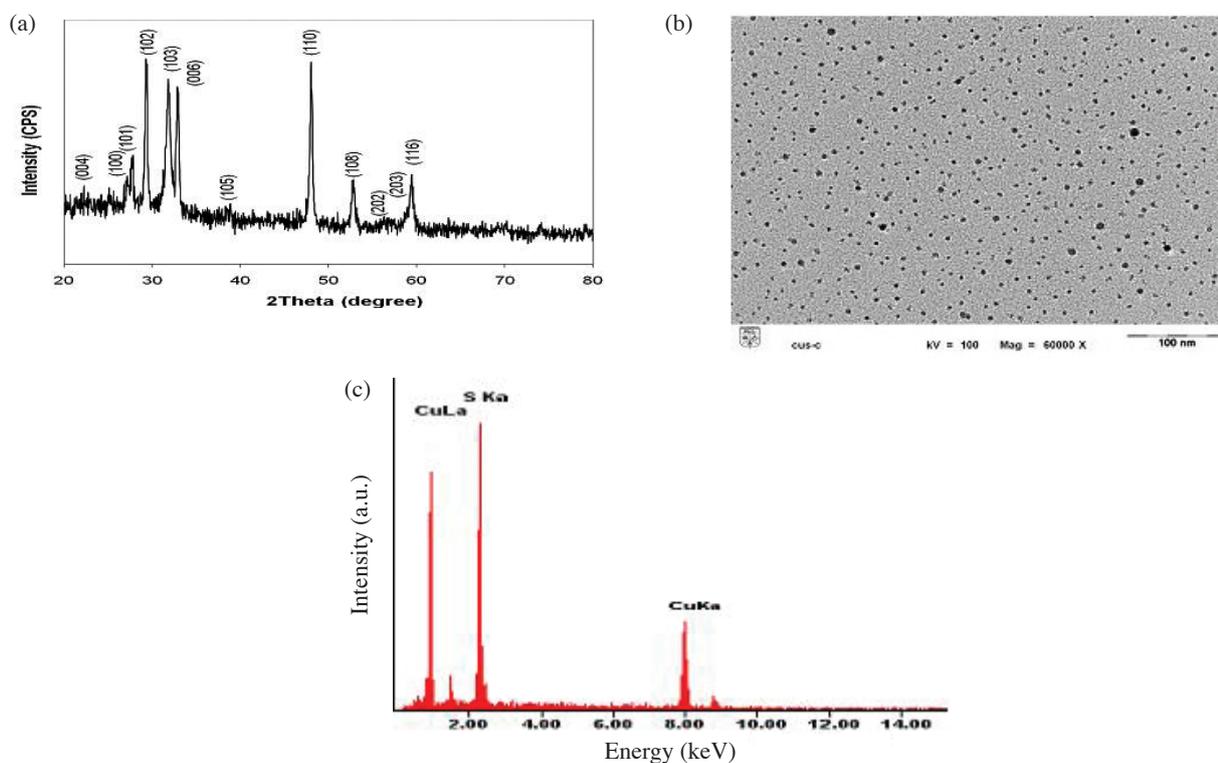


FIGURE 2. (a) XRD pattern of CuS nanoparticles with all the peaks indexed for the hexagonal covellite phase (JCPDS card 06-0464); (b) TEM image of CuS nanoparticles at 60000 $\times$  magnification; and (c) EDX spectrum of CuS nanoparticles

**Iron sulfide** The XRD pattern of the as-synthesized iron sulfide nanoparticles is shown in Figure 3a. All diffraction peaks could be indexed as cubic pyrite phase ( $\text{FeS}_2$ ) with a lattice constant of  $a = 5.42 \text{ \AA}$  (JCPDS Card No. 42-1340). The average particle size was determined as  $4.32 \pm 0.76 \text{ nm}$  (Figure 3b). The EDX spectrum (Figure 3c) shows the presence of oxygen and iron elements, revealing the expected composition of  $\text{FeS}_2$ .

**Molybdenum sulfide** Figure 4a shows the characteristic peaks of the rhombohedral phase molybdenite-3R,  $\text{MoS}_2$  (JCPDS Card No. 17-0744;  $a = 3.16 \text{ \AA}$ ,  $b = 3.16 \text{ \AA}$  and  $c = 18.33 \text{ \AA}$ ). The diffraction peaks are broad and weak, suggesting the nano-crystalline structure of the sulfide particles. This could be interpreted in terms of the requirement of further annealing on the as-prepared  $\text{MoS}_2$  particles for improving the degree of crystallinity of the particles as reported previously (Ma et al. 2008). Figure 4b illustrates the TEM image of the resultant particles. It can be seen that the particles were well dispersed with average particle size  $10.66 \pm 2.31 \text{ nm}$ . EDX analysis was also performed and the result (Figure 4c) proved that the resultant particles were  $\text{MoS}_2$  nanomaterial, which was consistent with the XRD pattern.

**Solvolytic liquefaction** A comparison of the yields of oil and gas in solvolytic liquefaction of soda lignin in ethylene glycol for 60 min with and without catalyst is shown in Figure 5. Generally, the addition of catalysts ( $\text{CuS}$ ,  $\text{MoS}_2$ ,  $\text{FeS}_2$ ) enhanced the formation of oil and

gas in temperature  $250^\circ\text{C}$  for reaction time, 60 min. The oil yield increased from 52.8% (without catalyst) to 65.16% (with 3 wt%  $\text{CuS}$ ). Meanwhile, for the yield of gas produced in Figure 6, the yield increased from  $472 \text{ cm}^3$  (without catalyst) to  $560 \text{ cm}^3$  (with 3 wt%  $\text{CuS}$ ),  $2890 \text{ cm}^3$  (with 3 wt%  $\text{MoS}_2$ ), and  $1550 \text{ cm}^3$  (with 3 wt%  $\text{FeS}_2$ ). As shown in the figures,  $\text{MoS}_2$  appeared to be more effective than other transition metal sulfide catalysts for promotion of the oil and gas formation within the tested temperature range. It might be generally concluded that the certain transition metal sulfide based catalysts can promote the oil and gas production.

The elemental compositions (C, H and N) of the oil were analyzed with an elemental analyzer, and the results for higher heating value were presented in Figure 7. The incorporation of  $\text{MoS}_2$  catalyst material led to a significant increment in higher heating value ( $26.44 \text{ MJ/kg}$ ) as compared to the soda lignin powder which was only achieved  $13.08 \text{ MJ/kg}$ . The result suggested that solvolytic liquefaction with catalyst especially  $\text{MoS}_2$  and  $\text{FeS}_2$  could be a promising technique to upgrade biomass feedstock or bio-waste with low heating values to liquid fuels with increased heating values.

## CONCLUSION

In summary, we have demonstrated a viable hydrothermal method for synthesizing transition metal sulfide nanoparticles using sodium thiosulfate, hydroxylamine sulfate, and transition metal salts as source materials

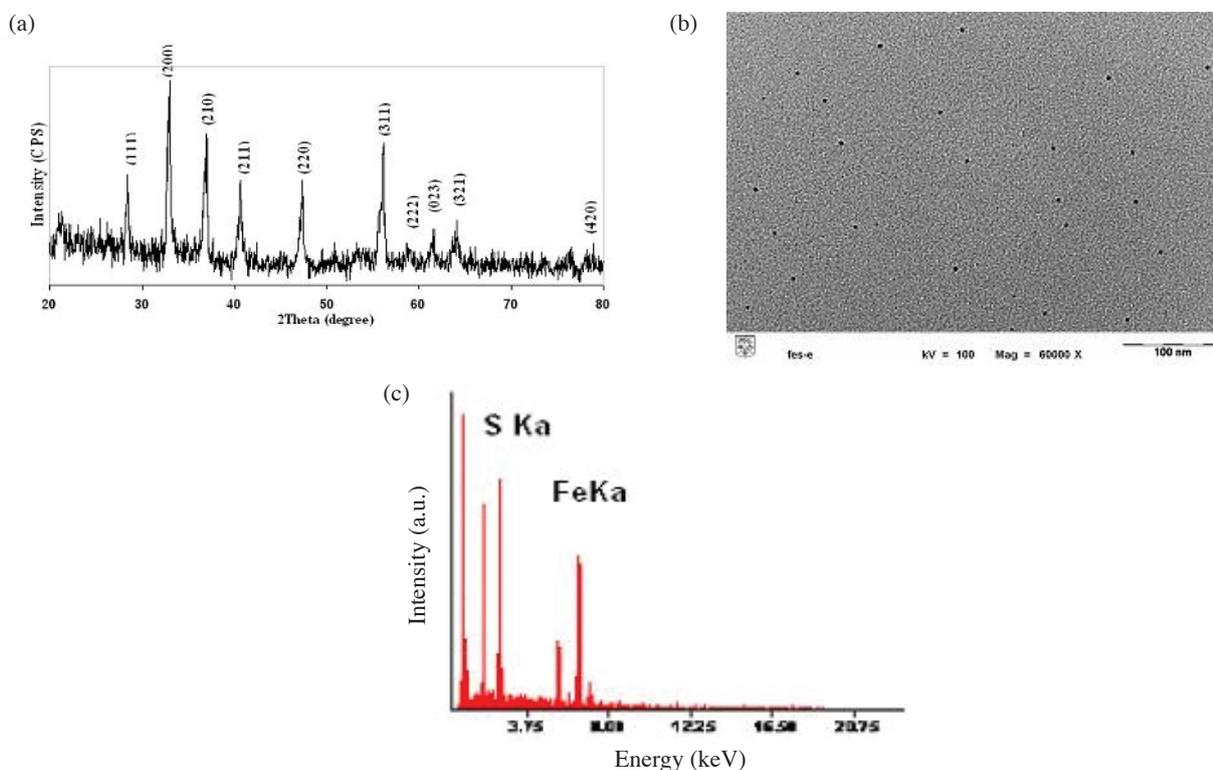


FIGURE 3. (a) XRD pattern of  $\text{FeS}_2$  nanoparticles with all the peaks indexed for the cubic pyrite  $\text{FeS}_2$  (JCPDS card 42-1340); (b) TEM image of  $\text{FeS}_2$  nanoparticles; and (c) EDX spectrum of  $\text{FeS}_2$  nanoparticles

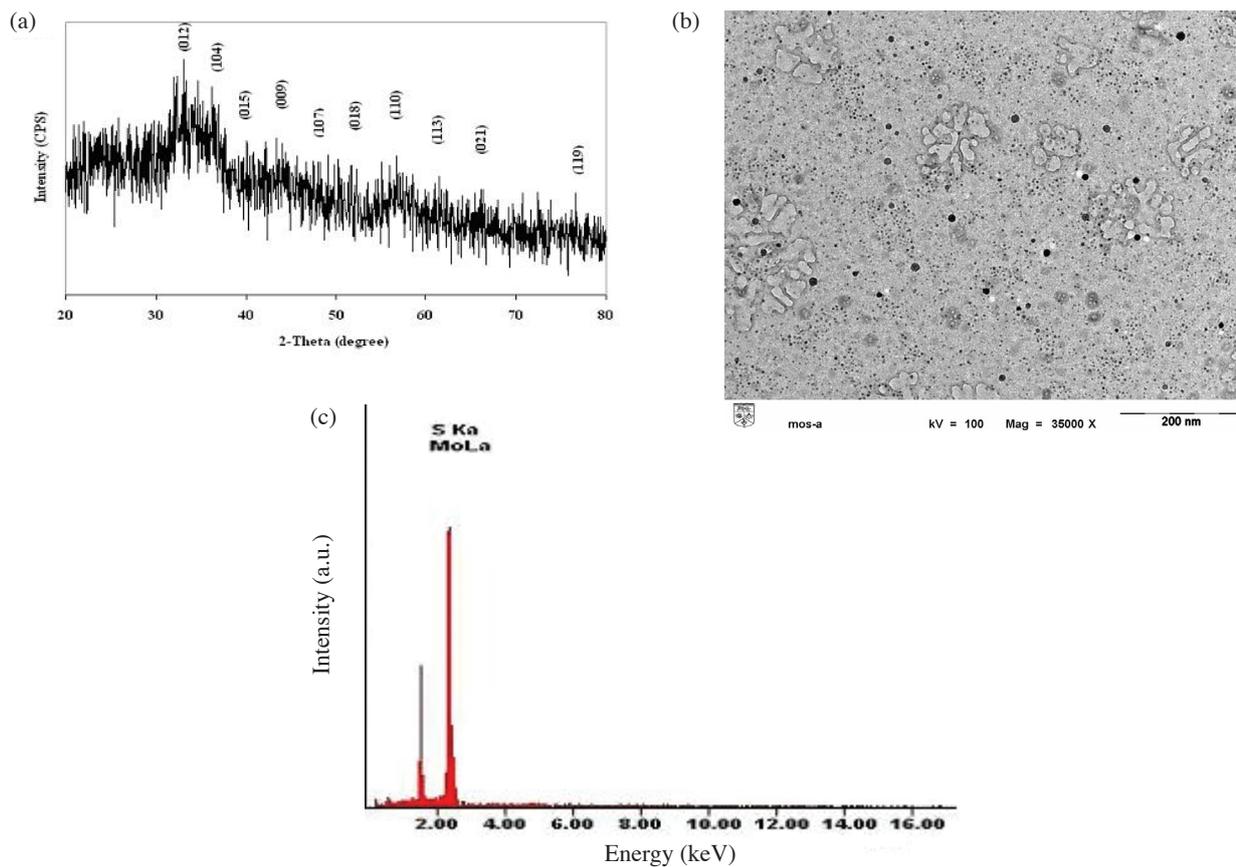


FIGURE 4. (a) XRD pattern of MoS<sub>2</sub> nanoparticles with all the peaks indexed for the rhombohedral molybdenite-3R (JCPDS card 17-0744) are shown for comparison, (b) TEM image of MoS<sub>2</sub> nanoparticles and (c) EDX spectrum of MoS<sub>2</sub> nanoparticles

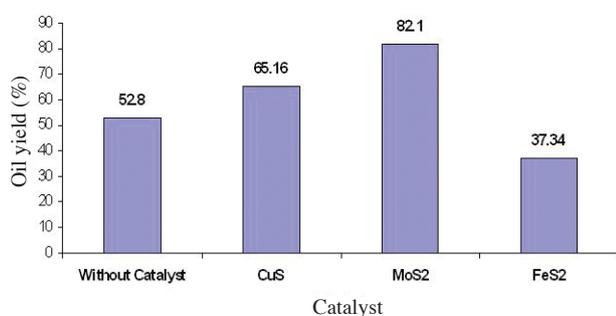


FIGURE 5. Yield of oil in solvolysis liquefaction of lignin in EG for 60 min with and without catalyst

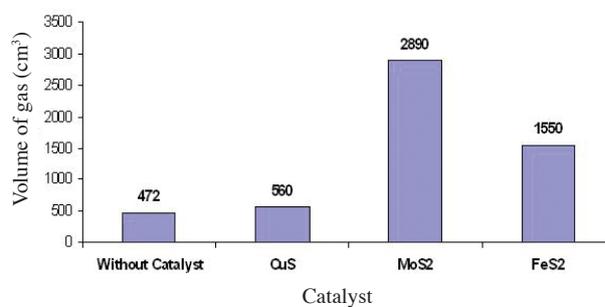


FIGURE 6. Volume of gas released in solvolysis liquefaction of lignin in EG for 60 min with and without catalyst

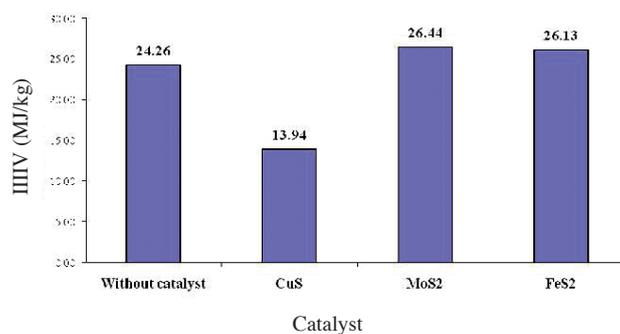


FIGURE 7. Higher Heating Value (HHV) of the oil from solvolysis liquefaction of lignin in EG for 60 min with and without catalyst

at 200°C for 90 min. By using this method, nano-sized hexagonal CuS, cubic FeS<sub>2</sub>, and rhombohedral MoS<sub>2</sub> could be successfully produced. The addition of transition metal sulfide based catalysts (CuS, MoS<sub>2</sub>, FeS<sub>2</sub>) during the liquefaction of soda lignin enhanced the yields of oil and gas and significantly increase the higher heating value of the oil products.

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