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RESEARCH PAPER

# Investigation on the reactivity of isopropanol with lignite-related model compound

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**Abstract:** The isopropanolysis of lignite model compound was investigated using the density functional theory method. Firstly, thermodynamic properties were estimated. Secondly, the method combined the Hirshfeld population and the Fukui function was proposed to obtain the initial reactant configuration. Thirdly, the Linear Synchronous Transit method combined with the Quadratic Synchronous Transit method was developed to calculate the reaction pathway and simultaneously optimize the structures of reactant and product. It was observed that the calculated enthalpy was decreased with increasing temperature. Furthermore, the nucleophilic group was discovered. Moreover, it was proved that the isopropanol was the most active among the common alcohols, indicating that the isopropanolysis was exothermic and nucleophilic.

**Keywords:** isopropanolysis; lignite; optimization; density functional theory; reaction mechanism

Lignite as fuel is uneconomic due to high ash yield, poor stability and low calorific[1]. In fact, there is high oxygen content in lignite. Therefore, many high value-added oxygen-containing chemicals can be obtained from lignite, which caused a wide range of concern[2].

Lignite degradation in the proper solvent is an important step to obtain the high value-added oxygen-containing chemical. It was reported that methanol, ethanol and isopropanol are effective solvents because of high hydrogen donating and alkylating abilities[3−5]. Therefore, many literatures of lignite degradation with alcohols have been published. Lei et al[6] studied the degradation behavior of Shengli lignite with methanol, and revealed that Shengli lignite had a good reaction activity. Kuznetsov et al[7] investigated the reactivity of Kansk-Atchinsk lignite with two lower aliphatic alcohols, and demonstrated that those alcohols (ethanol and isopropanol) were active. Further, the mechanism of lignite degradation had been investigated. First, it was found that the more soluble portion was obtained using branched alkanol than the straight one[8]. Lu et al[9] confirmed that the nucleophilic attack of the oxygen atom in alkanol took place in the degradation of Huolinguole Lignite, and proved that the nucleophilic reaction is crucial reactive step to produce the high value-added oxygen-containing chemical. In addition, it was reported that the radical formation was not involved in the alkanolysis[2]. Unfortunately, the mechanism of lignite degradation with isopropanol at the molecular level is rarely investigated.

The reaction mechanism at the molecular level was usually investigated using theoretical chemistry methods[10]. Among those methods, the density functional theory (DFT) was one of the most popular methods to explore the reaction mechanism at the molecular level[11]. However, the DFT method was completely based on a rigorous initial structure[12]. And then, the initial molecular structures were prominent during DFT calculation process. There were some ways to obtain information of the initial structures. Firstly, the number of electrons associated with the bond was obtained by using the Hirshfeld population analysis[13]. Then, the Fukui function method revealed the reactivity of a molecule with respect to electrophilic and nucleophilic attack on the charge density[14]. Combined two methods together, the relative configuration of reagents was acquired. However, the configuration using two above methods was coarse during the reaction mechanism investigation.

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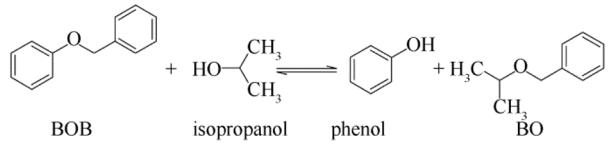


Fig. 1 Reaction of BOB and isopropanol

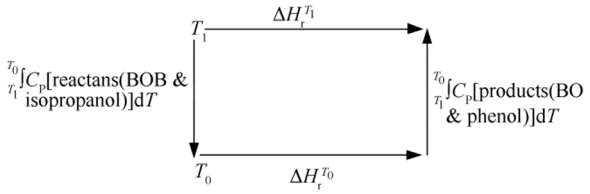


Fig. 2 Pathway of estimated Gibbs free energy $T_0$=0 K

Therefore, Linear Synchronous Transit (LST) combined with the Quadratic Synchronous Transit (QST)[15] was also proposed for optimizing reactant structure and simultaneously obtaining the transition state[16,17].

On the other hand, the thermodynamic properties reflected equilibrium characteristic of reaction[18], which was calculated based on the vibration analysis using DFT method[19–21]. It has been reported that the reaction enthalpies ($H$) related to three mechanisms of phenolic antioxidants action in gas-phase were calculated using the DFT method[22]. Similarly, values of entropies ($S$), free energy ($G$) and heat capacity at constant pressure ($C_p$) were also obtained with the DFT method. Based on the above datum, the equilibrium constant was then estimated[23]. However, literature including thermodynamic properties analysis and reaction mechanism of lignite degradation was seldom published.

Lignites have macromolecular structures and contain amounts of oxygen-containing moieties[24]. Lignin during the coal-forming process is an important moiety and underwent less change due to its structural stability[25]. Benzyloxybenzene (BOB) is an important moiety in brown coal, and was used as lignin structure model published by Adler[26]. In addition, BOB exists in macromolecular structure of lignite, and plays the significant role in coal conversion. Therefore, BOB was chosen as lignite-related model compound to study the characteristic of lignite isopropanolysis.

As the mentioned discussion, the reactivity of BOB and isopropanol was investigated in our work. First, thermodynamic properties of BOB isopropanolysis were estimated based on the vibration analysis using the DFT method. Then, the configuration of BOB and isopropanol was determined based on Hirshfeld electron and Fukui function. And, the improved method based on the LST/QST was carried out to obtain the transition state and simultaneously optimize structures of reactant and product.

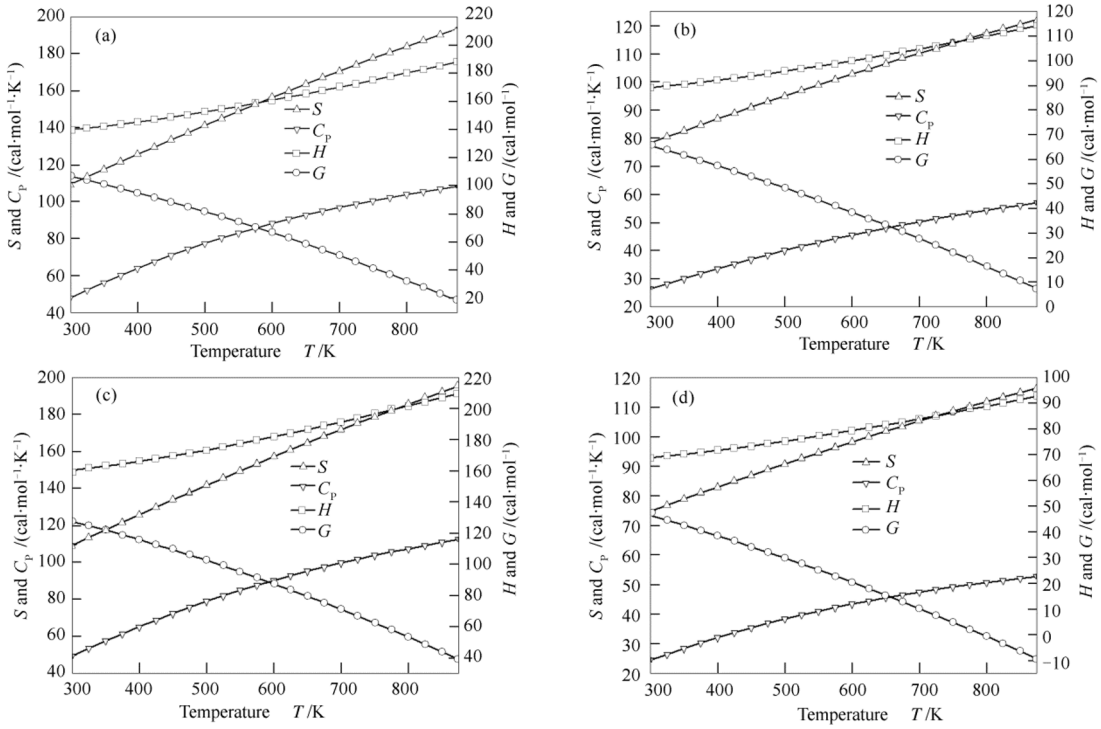


Fig. 3 Thermodynamic properties of components

(a): BOB; (b): isopropanol; (c): BO; (d): phenol