

# Study on the Effect of Addition of Amine Compounds on Coal Liquefaction(石炭液化反応に及ぼすアミンの添加効果に関する研究)

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## 論文内容要旨

### Chapter I Introduction

Coal has been used as an important source of fuel and raw material for producing chemicals for many decades. Research and development on coal liquefaction, i.e., conversion of coal into clean liquid fuels have been carried out to secure the supply of liquid transportation fuels. Coal liquefaction is carried out at elevated temperature under high hydrogen pressure in the presence of a catalyst and a hydrogen donor solvent. Liquefaction solvents have two main roles: (1) to stabilize coal radicals by donating hydrogen, and (2) to dissolve and/or disperse coal constituents. A good solvent should have these two properties for a better efficiency of liquefaction. However, there may be no ideal solvent, which has the both abilities. The use of an additive is one way to increase the efficiency.

This thesis deals with the study on the effect of amines as an additive on coal liquefaction. Amine compounds have a great possibility to affect coal liquefaction through their ability of dissolution, swelling, and surface activity for coal. However, there is little information on the effect of amines as an additive on coal liquefaction. The objective of this thesis is to clarify the effect of the addition of amines on coal liquefaction and mechanism of coal liquefaction in the presence of amines.

### Chapter II Liquefaction in the Presence of Primary Aliphatic Amines under Various Liquefaction Conditions

In this chapter, the effect of addition of primary aliphatic amines such as *n*-hexylamine on coal liquefaction under various conditions was investigated. Seven coals with different rank (C : 62.0-89.7 wt %, dry ash free (daf) basis) were used. All liquefaction experiments were performed in a 55 ml magnetically stirred autoclave, in which 3 g of coal, 6 g of solvent (tetralin or 1-metylnaphtalene), and 3 wt % (based on coal) of pyrite (FeS<sub>2</sub>) as Fe, in the case of catalytic liquefaction, were charged. Liquefaction was carried out under 9.7 MPa of hydrogen or nitrogen atmosphere. Liquefaction products were separated by using solvent extractions with tetrahydrofuran, toluene, and *n*-hexane under ultrasonic irradiation at room temperature. Liquefaction conversion was determined from the quantity of tetrahydrofuran insoluble residue (THFI). Oil was defined as *n*-hexane soluble fraction. Intermediate products, i.e., preasphaltene (PAS) and asphaltene (AS) were defined as tetrahydrofuran soluble/toluene insoluble fraction and toluene soluble/*n*-hexane insoluble fraction, respectively. Oil yield was determined by difference, i.e., conversion -

PAS – AS. Small amount of gases such as CO<sub>2</sub> and CO was also produced and was neglected in the evaluation of liquefaction products.

The addition of *n*-hexylamine increased the conversion of non-catalytic liquefaction at 400 °C for 10 min in tetralin/H<sub>2</sub> for all the coals of wide range of coal rank. Pocahontas No.3 coal gave the smallest increment in the conversion, i.e., from 10.0 to 10.5 %, and the highest increment in conversion was achieved for Blind Canyon coal, i.e., from 58.0 to 82.7 %. For catalytic liquefaction of Banko coal (C : 70.8 wt %, daf) with pyrite at 400 °C, the addition of *n*-hexylamine and *n*-dodecylamine also increased the conversion, particularly at the initial stage of liquefaction, i.e., at 1 min liquefaction. The conversion increased linearly with increasing the amount of amines. The increment of the conversion by the amines addition was greater at 350 °C (about 20 %) than that (about 6 %) at 400 °C, though the conversion at 350 °C was lower than that at 400 °C. For the both non-catalytic and catalytic liquefactions with pyrite of Banko coal, the increment in conversion by the addition of *n*-hexylamine and *n*-dodecylamine at the initial stage was mainly due to the increase in the intermediate fractions, i.e., PAS and AS, indicating that in the presence of amines the main reaction path was consecutive, i.e., from the coal to oil via PAS and AS. On the other hand, the direct formation of oil from coal was predominant for liquefaction of Banko coal in the absence of amine. It was also found that direct formation of oil might occur by using hydrogen of the coal itself through hydrogen shuttling mechanism, not by using external hydrogen sources, tetralin and/or hydrogen gas.

### Chapter III Liquefaction of Banko Coal in the Presence of Various Amines

In this chapter, liquefaction of Banko coal in the presence of various amines with different basicity and steric bulkiness was investigated to clarify the effect of kinds of amines on coal liquefaction. Following amines were used in this study ; (1) primary aliphatic amine : *n*-propylamine, *n*-hexylamine, *n*-dodecylamine, and *n*-octadecylamine; (2) secondary aliphatic amine: di-*n*-propylamine and di-*n*-hexylamine; (3) tertiary aliphatic amine: triethylamine and tri-*n*-butylamine, and (4) aromatic amine: aniline and diphenylamine.

It was found that for primary aliphatic amines with different alkyl chain length (C<sub>3</sub> to C<sub>18</sub>) and similar basicity, the conversion of catalytic liquefaction with pyrite in tetralin/H<sub>2</sub> at 400 °C increased to a similar extent, but the product distribution was quite different, particularly at the initial stage of liquefaction, where the longer the alkyl chain of the amine, the more AS and the less PAS. The different behavior of the amines in coal liquefaction was explained by the solubility enhancement of PAS by the addition of long alkyl chain amines. Separation of PAS from the coal networks by dissolution in the solvent prevents condensation reaction to coal networks and promotes decomposition into lighter fraction such as AS. This would probably occur to a larger extent when long chain amines such as *n*-octadecylamine were used.

From the steric bulkiness standpoint, the addition of less bulky amine would be expected to give higher conversion. However, the addition of bulky tertiary tri-*n*-butylamine and secondary di-*n*-hexylamine was found to give higher conversion of non-catalytic liquefaction in tetralin/H<sub>2</sub> at 300 – 450 °C for 30 min, compared to that less bulky primary *n*-dodecylamine. The addition of tri-*n*-butylamine gave the largest effect at 350 °C, i.e., the conversion increased from 33.1 to 59.7 %. Results of non-catalytic liquefaction at 400 °C for 1 and 10 min showed that the addition of weak basic amines such as aniline and diphenylamine gave smaller effects on the conversion than that of strong amines. It was found that the increment in conversion of non-catalytic liquefaction by the addition of amines was in the order of secondary amine = tertiary amine > primary amine > aromatic amine. This order is that of the strength of their basicity, not steric bulkiness.

The conversions of catalytic liquefaction with pyrite were found to increase by the addition of amines such as *n*-hexylamine, *n*-dodecylamine, and tri-*n*-butylamine. At 350 °C for 30 min, the addition of *n*-hexylamine increased the

conversion from 33.1 % for non-catalytic run to 47.8 %. Meanwhile, in the absence of *n*-hexylamine, the conversion for catalytic liquefaction reached 39.1 %. The highest conversion was achieved when pyrite was added together with *n*-hexylamine, i.e., the conversion reached 61.9 %. This suggests enhancement of catalytic activity of pyrite in the presence of amines.

#### **Chapter IV Mechanism of Coal Liquefaction in the Presence of Amines**

In this chapter, mechanism of coal liquefaction in the presence of amines was investigated. Namely, the roles of the amines in coal liquefaction were discussed from the swelling and solubility enhancement, and the change in the surface properties of coal by amines.

Swelling measurements of coal with and without the addition of amines at room temperature and 200 °C were performed. The results showed that the increment in swelling degree by the amines addition was not correlated with the increment in liquefaction conversion. For the amines with the same number of carbon atom (C<sub>12</sub>) primary *n*-dodecylamine has better ability to swell the coal than more bulky secondary di-*n*-hexylamine and tertiary tri-*n*-butylamine, but it gave lower conversion, suggesting that amine induced swelling was less important.

Basicity of amines was found to be more influential than their swelling ability for the increment in conversion by the addition of amines. Results of FTIR analyses of tetrahydrofuran insoluble fraction showed that peak intensity of OH groups at 3200 cm<sup>-1</sup> decreased to a larger extent for the fraction obtained from liquefaction with the addition of amines. The peak intensity of OH groups decreased inversely with the liquefaction conversion. This can be explained by that amines with strong basicity enhance solubility of coal by breaking non-covalent bonds (associates) in the coal through their interaction with acidic functionalities in coal such as phenolic OH.

Low rank Banko coal has many polar functionalities such as COOH and phenolic OH. Change in surface properties of coal is possible due to the adsorption of the amine on the coal surface, resulting in a better dispersion of pyrite on the coal surface, which enhances the activity of the catalyst. It is also possible that the addition of amine prevents agglomeration of coal leading to a better dispersion of coal in the liquefaction solvent and a better contact with pyrite. Enhancement of catalytic activity of pyrite in the presence of amines was explained by the change in coal surface properties by adsorption of amine, resulting in a better dispersion of pyrite on coal surface.

#### **Chapter V Conclusions**

In this chapter, the results and conclusions obtained were summarized.

# 論文審査結果の要旨

石炭液化技術の開発は流体燃料の安定供給という観点から重要である。本研究は高効率液化技術の確立を目的とし、石炭の液化反応に及ぼすアミン化合物の添加効果およびその作用機構について詳細に検討したものであり、全5章から構成されている。

第1章は緒論であり、本研究の背景及び目的を述べている。

第2章では、石炭の液化反応に及ぼす第一級脂肪族アミンの添加効果を検討している。石炭化度の異なる種々の石炭の液化反応において液化率が *n*-ヘキシルアミンの添加により増加することを見出し、アミンの添加効果の程度と用いた石炭の化学構造との関連について考察している。パイライトを触媒とした液化において、アミンの添加効果は液化の初期において特に顕著であり、液化率の増加は主としてプレアスファルテンやアスファルテンなどの中間成分の生成量の増加によるものであることを明らかにした。これらの結果からアミン存在下における液化反応が固体石炭→プレアスファルテン→アスファルテン→オイルという反応経路で逐次的に進行することが示唆された。

第3章では、塩基性度や立体的嵩高さの異なる種々の脂肪族及び芳香族アミンを用い、アミンの種類がインドネシア産バンコ炭の液化反応に及ぼす影響について検討している。無触媒液化におけるアミンの添加効果は塩基性度が強いものほど液化率が高くなり、立体的嵩高さにはほとんど依存しないことを明らかにしている。また、触媒を用いた液化に脂肪族鎖長は異なるが塩基性度はほぼ同じである種々の第一級脂肪族アミンを添加物として用いた場合、アミンの種類によらず液化率の増加は同程度であるが、液化生成物の分布はアミンの種類に大きく依存した。特に反応初期においは、脂肪族鎖長の大きいアミンほどアスファルテン収率が大きく、プレアスファルテン収率が小さいことを明らかにした。

第4章では、アミン存在下における石炭の液化反応機構について検討している。アミン添加による液化率の増加にはアミンの石炭を膨潤させる能力よりもアミンの塩基性度がより顕著に寄与していることを明らかにし、塩基性のアミンが石炭中のフェノール性水酸基やカルボン酸などの酸性官能基と相互作用し、石炭の液化溶媒への溶解性を向上させる機構を提出している。第3章で得られた脂肪族鎖長の生成物分布に及ぼす影響についてもアミンの石炭を溶解する能力の脂肪族鎖長依存性から説明できることを示している。また、アミンの添加により液化触媒の活性が向上することを見出し、これがアミンの吸着による石炭の表面特性の変化から説明できることを示した。

第5章は結論である。

以上要するに本論文は、石炭液化反応に及ぼすアミン化合物の添加効果を明らかにし、石炭の高効率液化反応プロセス開発への道を開いたものであり、石炭工学の発展に寄与するところが少なくない。

よって、本論文は博士（工学）の学位論文として合格と認める。