Coal Liquefaction with Molten Tin Catalyst under H_2/CH_4 and H_2/N_2 Atmospheres of Various Compositions

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Under atmospheres of various compositions of H_2/CH_4 and H_2/N_2 , coal liquefaction over a molten tin catalyst at 420°C and under the initial total pressure of 5 MPa was studied. Conversion to preasphaltenes (PA) and to oils (OL-1, -2) depended little upon the partial pressure of hydrogen (p_{H_2}). On the other hand, conversion to asphaltenes (AS) showed large dependence on p_{H_2} , indicating that AS was formed after the consumption of the hydrogen originally contained in the reactant coal. Conversions for all liquid products obtained under H_2/CH_4 atmosphere differed little from those obtained under H_2/N_2 atmosphere. However, the reaction carried out under an atmosphere containing methane yielded asphaltenes of lower molecular weights. Furthermore, yields of all gaseous products (C_2H_6 , C_3H_8 , C_4H_{10}) obtained under H_2/CH_4 atmosphere were larger than those obtained under H_2/N_2 atmosphere. These results suggested that methane was not always inert in the coal liquefaction reaction.

1. Introduction

Since CH_4 occupies a larger part of the gases produced in coal liquefaction, the economy of a liquefaction process depends a great deal upon whether CH_4 is available as a component of the recycling gas. Thus, it is desirable to clarify the role and behavior of CH_4 in coal liquefaction. Recent work of Cypres and Furfari¹⁾ was aimed at solving the above problems. Their results are interesting and reveal several important aspects of the CH_4 -Coal interaction. However our knowledge on this problem is still limited and further studies are necessary. Accordingly the present work has been undertaken. Coal liquefaction experiments have been carried out under atmospheres of various compositions of H_2/CH_4 and H_2/N_2 with special attention paid to the effects of CH_4 . Experimental results together with simple discussions on the effects of CH_4 on coal conversion are presented in this paper.

2. Experimental

Since the details of techniques for coal liquefaction over the molten metal catalyst have already been reported in an earlier paper²⁾, only an outline of the experimental procedure used here will be described.

Coal liquefaction was carried out using a high pressure autoclave (250 ml capacity), equipped with a magnetically driven stirrer, under the following conditions : coal=Shin-Yubari Coal (10 g; -100 mesh), catalyst=tin shots (50 g; guaranteed grade reagent; the catalyst is in a molten state under the reaction conditions), temperature= 420°C , atmosphere= H_2/CH_4 or H_2/N_2 of various compositions, the initial total pressure=5 MPa, stirring rate=150 r.p.m., reaction period=1 h.

Reaction products were separated into gases, liquids, and solids. The total amount of the gaseous products was determined volumetrically and then analyzed by gas chromatography. The liquid products and solid products were mixed with each other and fractionated into oils-1 (OL-1), oils-2 (OL-2), asphaltenes (AS), and preasphaltenes (PA) by hexane decantation and successive Soxhlet extractions with hexane, benzene, and tetrahydrofuran, respectively.

Molecular size distributions of the liquid and solid products were determined by gel permeation chromatography (GPC). Measurements were carried out using a JASCO Trirotor-III instrument equipped with four Shodex columns (two A-80Ms, A-802 and A-801 connected in series) and a RI detector. The amount and concentration of a sample were 50 μl and 5 wt% in tetrahydrofuran, respectively. The results were converted to molecular

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Fig. 1 Conversions for Liquid Products as a Function of the Initial Partial Pressure of Hydrogen

weight distributions using standard polystyrene calibrations.

3. Results and Discussion

3.1 Conversion for Liquid Products

Conversion for PA, OL-1 and that for OL-2 as a function of the initial partial pressure of hydrogen (p_{H_2}) in the atmosphere gas are shown in **Fig. 1-a**, **Fig. 1-b** and **Fig. 1-c**, respectively. Conversion for all products varied but little with p_{H_2} . Furthermore, conversion for PA, OL-1 and OL-2 in the reaction under H₂/CH₄ atmosphere was about the same as that for the corresponding ones in the reaction under H₂/N₂ atmosphere. Conversion for AS is separately shown in **Fig. 2**. The strong

Symbols are the same as in Fig. 1

Fig. 2 Conversions for Asphaltenes as a Function of the Initial Partial Pressure of Hydrogen

dependence on p_{H_2} of the conversion for this fraction is in sharp contrast to the weak dependence on p_{H_2} of the conversion for other liquid products (PA, OL-1, OL-2). It must also be pointed out that AS conversion depends little on whether the hy-

a : effects of gas composition
 p_{H_2} = 1.2 (A), 3.7 (B), 4.0 (C), 4.5 (D), 5.0 (E) MPa in methane. (Initial total pressure = 5.0 MPa).
 b : effects of diluent gas
 p_{H_2} = 1.2 MPa in methane (A), in nitrogen (A') ;
 p_H = 3.7 MPa in methane (B), in nitrogen (B').
 (Initial total pressure = 5.0 MPa).

Fig. 3 Effects of Reaction Atmosphere upon Molecular Weight Distributions of Asphaltenes

Fig. 4 Yields of Gaseous Products

drogen atmosphere is diluted with CH_4 or with N_2 .

The weak dependence on p_{H_2} of PA conversion probably indicates that PA is a product initially formed from the reacting coal. It is known³⁾ that at initial stage of coal liquefaction, the internal hydrogen is mostly consumed by a shuttling mechanism and the hydrogen present in the surrounding atmosphere is consumed but slightly. On the other hand, it is reported⁴⁾ that AS is formed mostly from PA. Since the internal hydrogen is already exhausted in forming PA, the hydrogen existing in the surrounding atmosphere must be consumed in forming AS. Thus, the strong dependence on p_{H_2} of AS conversion is reasonable.

Experimental results that conversion for every liquid products varied but little by changing the atmosphere gas from H_2/CH_4 to H_2/N_2 seemed to indicate that CH_4 acted as an inert gas like N_2 . However, the following experimental results caused us to suspect that this would not be the case.

3.2 Molecular Weight Distribution of AS Fraction

GPC elution curves for AS fractions obtained under different conditions are shown in Fig. 3-a indicating that the larger the p_{H_2} value the broader is the molecular weight distribution; also the larger the CH_4 content in the atmosphere gas, the smaller is the molecular weight of the corresponding AS product. It is also important that the molecular weight reducing effect of CH_4 is larger than that of N_2 , as indicated in Fig. 3-b. This clearly shows that CH_4 and N_2 behave differently in the coal liquefaction reaction.

3.3 Yields of Gaseous Products

Yields of ethane, propane, and butane are shown as a function of p_{H_2} in Fig. 4. It is seen that the dependence on p_{H_2} of the products obtained under H_2/N_2 atmosphere is larger than that of the products obtained under H_2/CH_4 atmosphere. In addition, yields of all gaseous products of the reaction under H_2/CH_4 atmosphere are greater than those of the reaction under H_2/N_2 atmosphere. These facts also show that CH_4 behaves differently from N_2 in the coal liquefaction reaction. It is known⁵⁾ that CH_4 can react with coal radicals existing in the flash pyrolysis of coal. Therefore, CH_4 has likely been incorporated into the gaseous products with carbon numbers higher than 2. If this is the case, the coal radicals would be stabilized and prevented from repolymerization, giving liquid products with smaller molecular weights as observed in the AS fraction (Fig. 3).

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要 旨

種々の組成の H_2/CH_4 および H_2/N_2 雰囲気下における
液体スズ触媒上での石炭液化反応

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石炭液化反応の雰囲気ガス中のメタンの影響を調べるため、種々の組成の H_2/CH_4 ガス雰囲気下で新夕張炭の液化を行い、 H_2/N_2 ガス雰囲気下の結果と比較した。ただし、反応温度は 420°C 、全圧は 5 MPa (初圧) と一定に保ち、触媒には液体スズを使用した。

液生成物のうち、プレアスファルテン (PA) と油分 (OL-1, 2) の収率は、雰囲気ガス中の水素分圧 (p_{H_2}) によって余り大きくは変化しなかった (Figs. 1a~c)。しかし、アスファルテン (AS) の収率は、 p_{H_2} によって大きく変化した (Fig. 2)。これらの結果と既往の知見を考慮すると、反応初期に石炭の保有水素のシャットリングで生成するのは、おそらく PA であり、AS は内部水素が消費されてから生成する 2 次的な留分と考え

られる。PA, AS, OL-1, 2 いずれの収率も、反応雰囲気が H_2/CH_4 であっても H_2/N_2 であっても実質的には変わりなかった (Figs. 1, 2)。このことは CH_4 が不活性ガスとして振舞うかのような印象を与えるが、主液生成物であるアスファルテン (AS) の平均分子量は、 H_2/CH_4 雰囲気下で得られた AS については、 CH_4 含有率を増すほど小さくなった (Fig. 3a)。そして、このような AS の平均分子量を低下させる効果は、 N_2 よりも CH_4 の方が大きかった (Fig. 3b)。さらに、ガス生成物 (C_2H_6 , C_3H_8 , C_4H_{10}) の収率は H_2/CH_4 雰囲気の方が H_2/N_2 雰囲気下よりも高い値となった (Figs. 4a~c)。これらのことは、石炭液化反応において、 CH_4 が必ずしも不活性とは言えぬことを示唆するように思われる。

Keywords

Asphaltene, Coal liquefaction, Hydrogen, Methane, Molten tin catalyst, Nitrogen