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# METHANOL REMOVAL FROM LPG AS PRETREATMENT OF CALORIFIC VALUE ADJUSTMENTS FOR LNG

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## 1. ABSTRACT

Basic design of a LPG purification system using a low temperature liquid phase adsorption method was investigated. In the present study, Na-X type zeolite was selected as the adsorbent for impurities in LPG, such as methanol and water. From the laboratory scale experiments and the numerical simulations, methanol and water were found to share adsorption sites on the Na-X type zeolite. In addition, methanol had a weaker adsorptive power than water. In the field test by bench scale experiments, the adsorption capacity and the mass transfer zone width of Na-X type zeolite for methanol, which is the key component of LPG purification, were measured and found to be 26 wt.% and 35 cm, respectively. The results obtained demonstrate adequate performance for design purposes of a practical system.

# TABLE OF CONTENTS

## 2. Introduction

In Tokyo Gas, natural gas, usually imported in liquefied form as LNG to Japan from abroad, is mixed with LPG at LNG terminals for calorific value adjustments to fulfill the stringent gas quality criteria set within 45 ± 1 MJ $m^{-3}$ for ensuring proper combustion properties for various gas appliances. Liquid/liquid calorific value adjustment is a method used for adding LPG to LNG, in which both LPG and LNG are maintained in the liquid phase to form a mixture under -150 degC. Then, mixture is vaporized and odorized for distribution as fuel gas through a pipeline network.

In the liquid/liquid calorific value adjustment process, impurities present in LPG, such as water and methanol, should be monitored carefully. In general, water contamination is originated from a process in which methanol is added to prepare solution for LPG production. Although both water and methanol are kept dissolved below -40 degC, they may precipitate in an LNG/LPG mixture even under -150 degC [1]. Once precipitation occurs, manufacturing apparatus and piping may suffer from blockage and other troubles; hence, it is necessary to remove these contaminants from LPG prior to mixing with LNG.

The main objective of the present research is to collect basic design data for a removal system of water and methanol. Having considered several purification processes, such as cryogenic separation and membrane technologies, liquid-phase adsorption using a Na-X type zeolite was chosen for a study employing the actual low-temperature LPG. The adsorption behavior of methanol and water on zeolite was investigated first on laboratory scale experiments. Larger scale field tests were then conducted to figure out the adsorption capacity and the width of adsorption band, known as mass transfer zone (MTZ). Numerical simulations were also carried out on characteristics of the adsorption sites affecting the zeolite activities.

## 3. Laboratory experiments and numerical simulations

### 3.1. Laboratory experiments

#### 3.1.1. Experimental methods

The adsorption behavior of methanol and water on a Na-X type zeolite was investigated in the laboratory. Figure 1 shows a schematic of the experimental apparatus. Gaseous propane at the ambient temperature and pressure was used. Methanol and water content in the gaseous propane was adjusted to 300 and 40 wt. ppm respectively. It was made by mixing of propane saturated with water and the other with methanol and then diluting with pure propane. The total flow rate was 200 mL $min^{-1}$. The concentration of methanol and water in the gas flowing through the inlet and the outlet was measured continuously using the mass spectrometer.

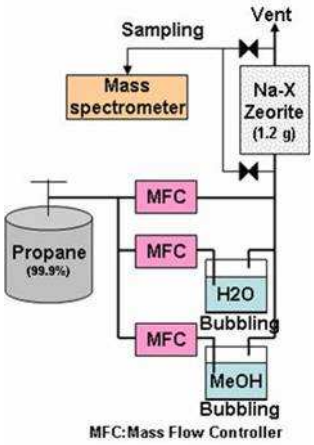


Fig. 1 Schematic of the experimental setup.

### 3.1.2. Results and discussion

In the adsorption breakthrough curves shown in Fig. 2, adsorption by the Na-X type zeolite has been confirmed for both methanol and water. The total operation times until the breakthrough of methanol and water were 2 and 10 hours, respectively. The breakthrough time for methanol was found to be shorter than that of water; hence, methanol was found to be less adsorbable than water onto the Na-X type zeolite surface. This result can be explained by comparing the molecular size of the adsorbates; since molecules of water are much smaller than methanol's, they can easily diffuse into the Na-X type zeolite structure and adsorb on it. Thus, breakthrough of water was detected after methanol breakthrough had been observed.

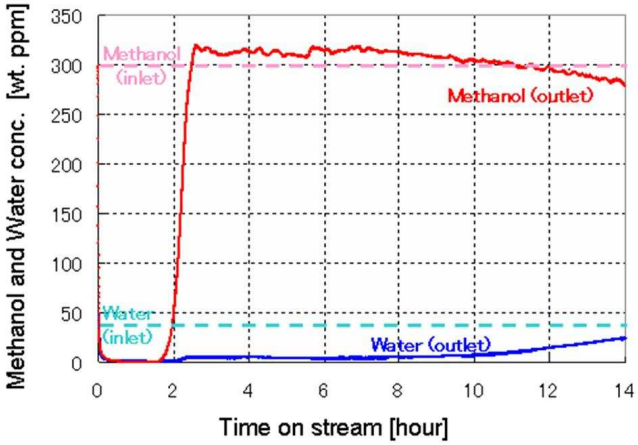


Fig. 2 Breakthrough curves for methanol and water adsorption.

### 3.2. Numerical simulations

### 3.2.1. Calculation conditions

The laboratory test showed that the adsorbability of methanol is lower than that of water at the ambient temperature and pressure. Numerical simulations were conducted to make comparison in low-temperatures and high-pressures; namely, under the realistic conditions. The equilibrium adsorption capacity of methanol and water on a Na-X type zeolite was studied using a Monte Carlo simulation technique available in a commercial software package, “Material Studio 5.0” (Accerlys, Inc.). The calculation conditions are shown in Table 1. In Runs #1 and #2, only methanol and water existed in propane, respectively. While in Run#3, both methanol and water were present. Furthermore, the simulations provided information on adsorption sites of each molecules on a Na-X type zeolite.

Table 1 Calculation results of equilibrium adsorption capacity. (at 0.5 MPa and -40 degC)

| Run# | Concentration of adsorbate | Equilibrium adsorption capacity | |
|---|---|---|---|
| | | Methanol | Water |
| 1 | Methanol 200 wt. ppm | 29 wt. % | - |
| 2 | Water 200 wt. ppm | - | 43 wt. % |
| 3 | Methanol 200 wt. ppm and Water 200 wt. ppm | 11 wt. % | 30 wt. % |

### 3.2.2. Results and discussion

The results of the equilibrium adsorption capacity are provided in Table 1. Comparing the result of Run#1 with that of #2, it is evident that methanol possessed a smaller adsorption capacity than water. When water coexisted (Run#3), the adsorption capacity of methanol was degraded substantially.

The results of adsorption sites are also graphically represented in Figs. 3 and 4. Figure 3 shows the result in the absence of water (Run#1), while in Fig. 4 water was coexisting. The markers colored in red and blue respectively represent the adsorption sites of methanol and water. The obtained

results suggest that methanol and water components might have shared the adsorption sites. Furthermore, methanol desorption might also have taken place in competing with water adsorption. Focusing attention on the propane molecules (the black markers in Figs. 3 and 4), it is seen that the adsorption sites of propane in Fig. 3 (without water) were replaced by those of other molecules in Fig. 4 (water coexisting).

It should be noted that zeolites strongly adsorb the highly polarized molecules. As the polarity is much higher in water than methanol, water is likely to be adsorbed more on the Na-X type zeolite than methanol. In contrast, propane, as non-polar molecules that can be hardly adsorbed, is easily desorbed when adsorbable molecules are coexisting.

From the results of the laboratory experiments and the numerical simulations, it may be concluded that adsorbed methanol on the Na-X type zeolite will be replaced by water under the condition investigated. These results indicated that under the actual conditions, the adsorption capacity of methanol may be expected to reach on practical levels (e.g., higher than 10 wt. %), despite of its lower adsopbability compared to water. Note that in the actual situations, the concentration of methanol in LPG is usually much higher than water's. Consequently, methanol adsorption characteristics are thought to be the crucial factor for controlling adsorbent performance.

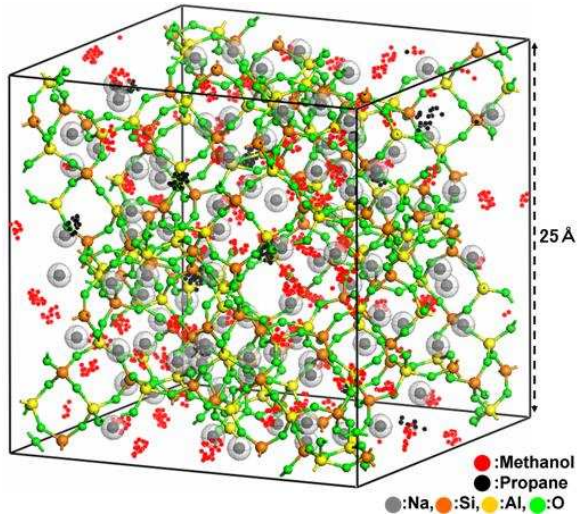


Fig. 3 Adsorption sites of methanol and propane in the absence of water.

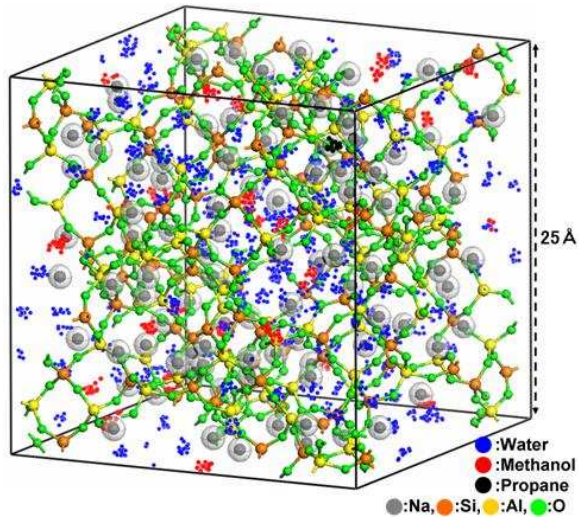


Fig. 4 Adsorption sites of water, methanol and propane when water coexists.

## 4. Field Tests

### 4.1. Experimental methods

From the results of the laboratory experiments and the computer simulations discussed earlier, water was found to be more adsorbable than methanol onto the Na-X type zeolite surface in the ambient temperature. While the adsorption capacity of water in LPG has been known to be about 25 wt. % at -20 degC in our previous study, there appears to be no measurements reported for that of methanol under a similar condition. Therefore, a series of field tests were conducted to determine the adsorption capacity and the band width of MTZ of methanol on a Na-X type zeolite, using actual low-temperature LPG at approximately -30 degC.

Figures 5 and 6 show a schematic and the appearance of the field test equipments, respectively. The test plant was constructed at the Tokyo Gas Sodegaura LNG terminal. There, adsorptive removal of methanol was studied using low-temperature LPG inflow at a predetermined methanol concentration, which was directed into the adsorption towers filled with a Na-X type zeolite. Part of LPG was drawn from sampling ports located at various heights of the adsorption towers, and measurements were taken of the vertical distribution of methanol concentration using a FID gas chromatography technique. The two adsorption towers, referred to as Towers A and B, of different sizes were employed under the basic test condition, as summarized in Table 2.

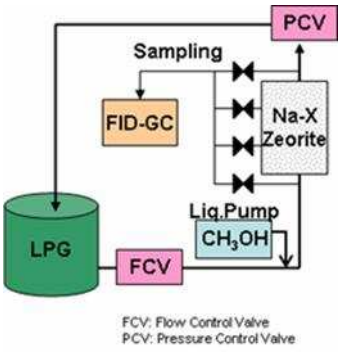


Fig. 5 Schematic of the field test equipment.


Fig. 6 Overview of the field test setup.

Table 2 Basic condition of the field tests.

| | Tower A (1/200 Scale) | Tower B (1/10 Scale) |
|---|---|---|
| Tower Size | $\phi$ 0.1 m, h 1.0 m | $\phi$ 0.5 m, h 0.3 m |
| Weight of Adsorbent | 4.9 kg | 35 kg |
| LPG flow rate | 120 kg $hour^{-1}$ | 1400 kg $hour^{-1}$ |
| LV of LPG | 50 cm $min^{-1}$ | 24 cm $min^{-1}$ |
| Methanol conc. | 200 wt. ppm | 200 wt. ppm |
| Pressure | 0.5 MPa | 0.5 MPa |
| Temperature | -35 degC ~ -25 degC | -35 degC ~ -25 degC |

### 4.2. Results and discussion

Figure 7 shows breakthrough curves of methanol for Tower A. For the first 6 hours of the operation, the methanol concentration at 30 cm high stayed below 1.0 wt. ppm, a level far lower than that of methanol frost (10 wt. ppm) present in the LNG-LPG mixture. After 6 hours, methanol breakthrough appeared to start and, by reaching 16 hours, the methanol concentration rose almost to that of LPG near the inlet. At 60 cm, breakthrough set in at around 18 hours and completed by 28 hours. Such breakthrough lasting about 10 hours remained almost the same regardless of sampling heights, as indicated by similar patterns in a set of breakthrough curves. The adsorption capacity of methanol may be calculated from the progression rate of the breakthrough curves in the flow direction and the total input of methanol inflow to become approximately 26 wt. %. An almost identical adsorption capacity was obtained in the numerical simulations mentioned in Table 1 (see the result of Run #1).

In addition, the breakthrough curves in Fig. 7 illustrate the methanol saturation on the Na-X type zeolite. The concentration of methanol at 30 cm high reached almost on the inlet level after 25 hours' operation. Since the packed Na-X type zeolites in the frontal part of the tower were mostly saturated with methanol, further methanol adsorption would not take place. The methanol concentration at 60 cm high rose to about 40 % of the inlet value by 25 hours, suggesting that almost 40 % of the available adsorption sites had been saturated with methanol. At the 70cm level, methanol is seen to start increasing after 25 hours; it is thought that the majority of adsorption sites were still free of methanol there. Figure 8 was obtained by plotting the degree of methanol saturation on the Na-X type zeolite at each height of adsorption tower. The transient area of methanol saturation at the height from 40 cm to 75 cm is called mass transfer zone (MTZ). From the result, the MTZ band width has been determined to be 35 cm for a linear velocity (LV) of 50 cm $min^{-1}$. Therefore, it can be said that the adsorption equilibrium of methanol may be easily reached. For higher LVs, methanol molecules are likely to elute off downstream without being much adsorbed by the Na-X type zeolite, possibly broadening the MTZ band width. On the other hand, the sufficiently high diffusivity of methanol would act to retain the band width. Since it is often seen that MTZ is proportional to the LV [2], its band width may turn out to be over several tens of centimeters on comparable LV levels considered here and it is sufficiently narrow for design purposes of a practical system.

Figures 9 and 10 are the results obtained from the scale up experiments using Tower B for the breakthrough curves of methanol and the MTZ band width, respectively. From Fig. 9, the adsorption capacity is determined to be 26 wt. %, while Fig. 10 shows the MTZ band width to be 35 cm. Due to the similarities in the results previously found for Tower A, it may be safely concluded that these properties should be fairly insensitive to scale up factors. The baseline data required for designing an appropriate purification system in a realistic pretreatment facility of calorific value adjustments for LNG were obtained in the present investigation.

Based on the data obtained for an adsorption capacity of 26 wt. % with a MTZ band width of 35 cm, basic design has been attempted as an example of the realistic purification system and the results are presented in Fig. 11. Assuming the mixing ratio of LPG for calorific value adjustment of $1 \times 10^7$ $m^3$ fuel gas to be 5 vol.%, impurities to be removed will amount to 25 kg. Hence, the adsorbent required is calculated to be approximately 100 kg in weight or 140 L in volume if the density of Na-X type zeolite is 0.7 kg $L^{-1}$. The basic design of the adsorption towers depicted in Fig. 11 is so planned that by aligning adsorption towers in series, towers located downstream can work to adsorb impurities in the MTZ band even if those upstream have reached the breakthrough point.

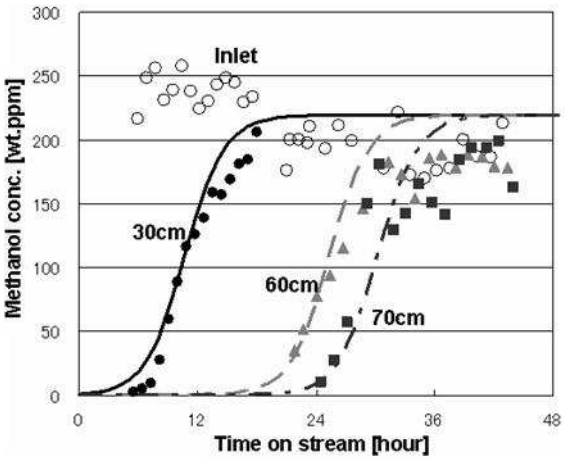


Fig. 7 Breakthrough curves for methanol adsorption for Tower A.

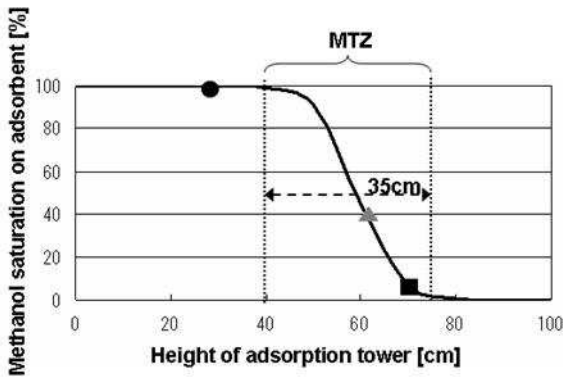


Fig. 8 MTZ of methanol adsorption for Tower A.

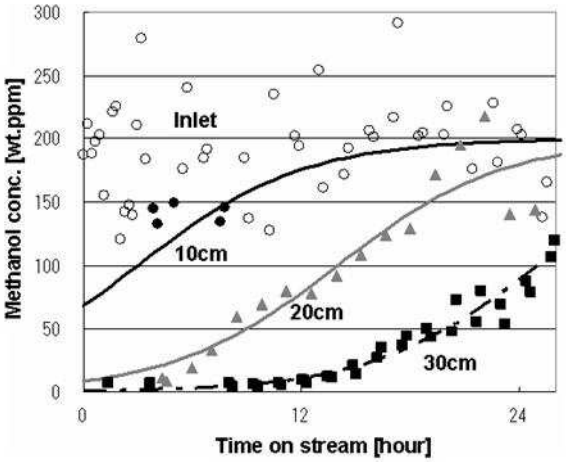


Fig. 9 Breakthrough curves for methanol adsorption for Tower B.

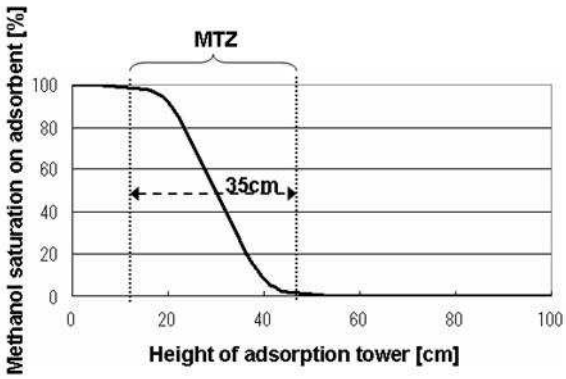


Fig. 10 MTZ of methanol adsorption for Tower B.

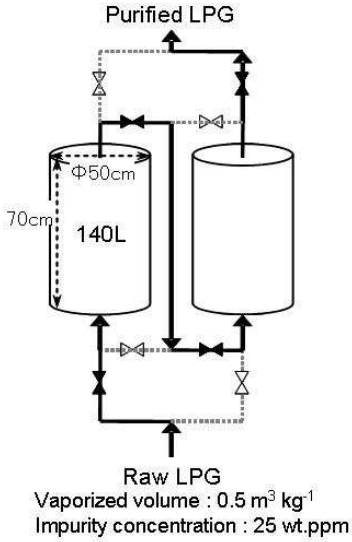


Fig. 11 Basic design of LPG purifier system for manufacturing $1 \times 10^7$ $m^3$ fuel gas.

## 5. Conclusions

By applying a Na-X type zeolite as adsorbent, methanol and water present in LPG may be sufficiently removed to meet the LPG quality requirement of liquid/liquid calorific value adjustment. The laboratory-scale experiments and the numerical simulations confirmed that both methanol and water were adsorbed onto the Na-X zeolite surface. Furthermore, adsorbent performance was largely governed by the behavior of methanol. In the succeeding field tests, the obtained adsorption capacity of methanol was found to be 26 wt. %, which will be sufficiently high when it is applied to a full-scale LPG purifier. In addition, MTZ band width was sufficiently narrow for design purposes of a practical system. As a design example on a practicable scale, 100 kg (140 L) of adsorbent is capable of purifying LPG to produce $1 \times 10^7$ $m^3$ of fuel gas. Further investigations focusing on design of a practical system and detailed operational issues may be thought to remain as the possible future task.

## 6. References

[1] Natural gas introduction promotion center (1988~1992). Development survey reports of calorific value adjustment of LNG.
[2] Takeuchi, Y., et al. (1999). Handbook of adsorption technologies, NTS Inc.

## 7. List of Tables



## 8. List of Figures