Steam Gasification of Residual Oils with Potassium Catalysts[†]

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This review paper is concerned primarily with the activity of potassium catalyst and the reaction path of the catalytic gasification with steam. The activity test of various potassium compounds, effect of potassium content on gas yield, X-ray diffraction patterns of β'' -alumina before and after the reduction of K, and the results of TG analysis of K_2SO_4 showed that the catalytically active component was not potassium compound, but metallic or cationic potassium. From the experimental results on steam gasification of activated carbon mixed with alumina supported K_2CO_3 , it is deduced that potassium migrates readily to the carbon surface, and forms an unstable potassium-carbon complex which reacts with steam. Catalytic gasification continues until all potassium is consumed.

1. Introduction

It is well known that basic catalysts such as alkali or alkali earth compounds are effective for steam gasification of residual oils. Among these compounds, calcium oxide and potassium polyaluminate(β'' - Al_2O_3) are typical and practical. A number of papers on steam gasification with calcium oxide, dolomite and potassium polyaluminate have been reported by the author^{1)~10)}. Since, a review paper on steam gasification of residual oils in fluidized bed of dolomite and calcium oxide has already been published in J. Japan Petrol. Inst.⁴⁾. So, this paper will concern with a review of more recent reports^{9),10)} on potassium catalysts, including some original ones.

Although potassium catalysts have often been studied on the gasification of carbonaceous materials such as graphite, char and coal, little have been known about their catalytic effects on gasification of petroleum distillates and residues. This study will also concern with the catalytic properties of potassium supported on alumina. A fluidized bed reactor was used, because gasification of the residual oils in a fixed bed reactor produced so much tar and carbonaceous matters that it was difficult to make a fundamental study.

2. Experimental

2.1 Feedstock

Table 1 shows the specifications of the five

kinds of residual oils used in this experiment. To prepare heavier feeds, a SDA residue (*n*-pentane extraction raffinate) of Khafji vacuum residue was added in various amounts to the original feedstocks. Activated carbon used for a feed material was obtained from Tsurumi Coal Co., Ltd., and its analytic data in weight was C 95, O 1.7, H 0.3, N 0.1, S 0.1, ash 2.8.

2.2 Catalyst

CaO catalyst on α -alumina was prepared by calcination at 950°C for 4 hrs. Potassium polyaluminate was obtained from Kyushu Refractory Co. Ltd., and its approximate formula was $K_2O-5Al_2O_3$. The potassium polyaluminate catalysts with a smaller potassium content were prepared by removing part of the potassium from the original polyaluminate with an aqueous solution of nitric acid. The potassium content (C_K) in the catalyst was determined by flame photoanalysis and defined as follows.

$$C_K = \frac{\text{amount of K in the HNO}_3 \text{ treated catalyst (mg)}}{\text{amount of K in the original catalyst (mg)}}$$

Other catalysts were prepared by impregnating the alumina support and drying. The alumina support obtained by calcination of γ -alumina at 1,200°C for 2 hrs was dipped in an appropriate aqueous solution of an alkali metal compound, and dried at 110°C. Catalyst concentration was expressed in terms of the alkali metal or calcium oxide by weight. The catalyst was calcined at 350°C for 2 hrs and screened. Catalyst particles in the range of 32-65 mesh were used in the study. The catalytic activity was expressed in

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Table 1 Specifications of Feedstocks

Samples	Symbol	Ultimate Analysis (wt%)			C.C.R.*b) (wt%)	f _a *c)
		C	H	S		
Arabian Light (atmospheric residue)	A/L atmo	85.2	11.6	3.1	8.4	0.31
Iranian Heavy (atmospheric residue)	I/H atmo	85.6	11.4	2.7	10.7	—
Arabian Light (vacuum residue)	A/L vac	85.3	10.6	3.9	17.7	0.36
Arabian Medium (vacuum residue)	A/M vac	84.2	10.3	5.5	18.3	—
Khafji SDA* _a) (residue)	Kh SDA resid	82.3	7.9	7.3	34.1	0.47

*a) Solvent used in extraction is *n*-pentane.
*b) C.C.R. is the value of Conradson Carbon Residue.
*c) f_a value is the ratio of aromatic carbon to total carbon (according to the method of Speit).

Fig. 1 Schematic Diagram of Reactor Assembly

terms of the product gas volume and (CO+CO₂) yield.

2.3 Apparatus and Procedure

A fluidized bed reactor was used at atmospheric pressure. The schematic diagram of the reactor assembly is shown in Fig. 1. The reactor was a stainless steel tube of 40 mm diameter and 400 mm length. Alumina beads (3—4 mm diameter) were packed in the conical section of the reactor as catalyst support and gas distributor. Feedstock residue was introduced with steam at the bottom part of the fluidizing catalyst bed. To prevent coke plugging in the feed pipe, the atomizer was cooled by circulating a coolant. Steam for fluidization was supplied to the fluidized bed at the bottom side of the reactor. The catalyst was heated to gasification temperature in a stream of nitrogen and then reaction was started. After the removal of unreacted steam and a trace of oily products in an ice trap, and solid products such as soot in a solid remover, the product gas was passed through a solution of zinc amine complex

Fig. 2 Comparison of Catalytic Activity between β'' -Alumina and CaO(30%)-Al₂O₃

to absorb hydrogen sulfide. The product gas composition was determined by gas chromatography after the volumetric flow rate was measured. Using argon as a carrier gas, chromatographic separation of CO₂, H₂, CO, CH₄ was made with activated carbon and that of C₂H₄, C₂H₆ with alumina. To investigate the reduction of the catalysts, thermogravimetric analysis was performed using Shimazu thermal analyzer DT-30. Measurements were carried out under atmospheric pressure. The sample was heated at a rate of 10 °C/min in a stream of H₂, CO or He.

3. Results

3.1 Comparison of the Catalytic Activities of Calcium Oxide and Potassium Polyaluminate

As mentioned above, calcium oxide and potassium polyaluminate are outstanding catalysts for steam gasification of residual oils. To know char-

Table 2 Catalytic Activity of Potassium Catalysts and Product Gas Composition (Feedstock : A/L atmospheric residue (72.0 g/hr), Reaction temperature : 900°C, Molar H₂O/C : 1.2, Catalyst weight : 200 g)

Catalyst (10 wt% K-Al ₂ O ₃)	KCl	K ₂ CO ₃	K ₂ SO ₄	K ₂ PO ₄	KOH	β''-Al ₂ O ₃ *a)
Product Gas Volume (Nm ³ /kg-oil)	2.59	2.70	4.00	3.07	3.17	4.01
Gas Yield (%)	75.6	93.9	94.0	86.9	88.4	94.7
Gas Composition (vol%)						
H ₂	55.3	60.1	62.6	56.2	56.6	62.9
CO	21.2	29.0	30.7	25.2	24.3	31.5
CO ₂	9.8	3.9	3.0	8.0	8.6	2.5
CH ₄	11.9	6.5	3.7	9.2	9.5	2.7
C ₂ H ₆	0.1	—	—	0.1	—	0.1
C ₂ H ₄	1.7	0.5	—	1.3	1.0	0.4

*a) K : 13 wt%

○ : β''-Alumina, ● : CaO (30%) - Al₂O₃
Reaction temp. : 900 (°C), Steam ratio : 1.2
(H₂O mol/C mol), Feed oil : A/L atmo.

Fig. 3 Variation of Catalytic Activity with Time

acteristic differences of both catalysts, several studies have been made. **Fig. 2** shows the most remarkable result which was obtained when C/H ratios of the feeds changed. With increase of C/H, the activity of CaO catalyst decreased, but that of potassium polyaluminate remained.

Fig. 3 shows the activity change of both catalysts with time of reaction. The value of gas yield began to decrease at 4 hrs by CaO catalyst, and was constant for 8 hrs by potassium polyaluminate. This effect depended on the amount of carbon deposition on the catalyst.

Figs. 2 and 3 show that the potassium polyaluminate is more effective than the calcium oxide for steam gasification of low grade carbonaceous feeds. Therefore, the influence of K content on gasification has been pursued.

3.2 Effect of K Content in Potassium Polyaluminate

By treating potassium polyaluminate with aqueous HNO₃ solution, several catalysts of different potassium content were prepared and examined. As shown in **Fig. 4**, a notable relation was found between catalytic activity and potassium content.

Catalyst : β''-Alumina, Reaction temp. : 900 (°C), Feed oil : A/L atmo, Steam ratio : 1.2 (H₂O mol/C mol),

The amount of K in the
HNO₃ treated catalyst (mg)
 $C_K = \frac{\text{The amount of K in the}}{\text{The amount of K in the}} \times 100$
original catalyst (mg)

Fig. 4 Effect of K Content on Gas Yield

The X-ray diffraction patterns of these catalysts were identical with the pattern of β''-alumina⁵⁾. From the result, it was presumed that the activity of catalytic gasification did not depend on the potassium compound itself, but on potassium or potassium cation.

3.3 Activities of Various Potassium Compound

Although potassium polyaluminate maintains high activity for a long period, its chemical structure is too complicated to allow fundamental studies on gasification catalysis; so, simple potassium compounds have been used in this study. The results are listed in **Table 2**. While K₂CO₃, K₂SO₄, KOH and K₂PO₄ were found to be comparably active, KCl was less active. The reason of less activity would depend on the difficulty of reduction to potassium. β''-alumina showed the best result, but its chemical structure, K content and preparation method differed from those of the other catalysts.

The catalytic activities of K₂CO₃ and K₂SO₄

Feedstock : A/L atmospheric residue (72.0 g/hr),
Molar $\text{H}_2\text{O}/\text{C}$ ratio : 1.2, Catalyst weight : 200 g

Fig. 5 Effect of Reaction Temperature on Gas Yield

I : A/L vac. resid. + Kh. SDA resid. 10 wt%
II : A/L vac. resid. + Kh. SDA resid. 20 wt%
III : A/L vac. resid. + Kh. SDA resid. 30 wt%
Reaction temperature : 900°C, Oil feed
rate : 72.0~75.8 g/hr, Molar $\text{H}_2\text{O}/\text{C}$
ratio : 1.2, Catalyst weight : 200 g

Fig. 6 Effect of C/H Ratio on Gas Yield

are shown in **Fig. 5** as a function of gasification temperature. In the range of 850–950°C, their activities increased with temperature within the limits of experimental errors.

Both of these salts showed similar high activities for catalytic gasification of several residues with C/H ratios in the range 7.3–8.6, as shown in **Fig. 6**. The catalytic activities of both salts were similar and almost unchanged in the whole range of C/H ratio, despite the considerable difference of the properties such as aromaticity of the feeds.

3.4 Reducibility of K_2SO_4

As there was no appreciable difference in the catalytic effect between K_2CO_3 and K_2SO_4 , the reducibility of K_2SO_4 was studied to elucidate the catalytic behavior of these salts. **Fig. 7** shows TG curves for K_2SO_4 on alumina. Although K_2SO_4 on alumina was stable in He in the temperature range studied, the weight loss in K_2SO_4

A : Heating in atmosphere of flowing H_2 at 1 cc/sec
B : Heating in atmosphere of flowing CO at 1 cc/sec
C : Heating in atmosphere of flowing He at 1 cc/sec
Rate of temperature increase : 10°C/min

Fig. 7 Thermogravimetric Analyses with Respect to the Reduction of K_2SO_4 (K : 10 wt%) - Al_2O_3 Catalyst

was measurable above 650 and 750°C in the presence of H_2 and CO, respectively. The weight loss suggested that K_2SO_4 could be converted to K_2S in both of these reducing gases. It was also found that K_2SO_4 was reduced to K_2S by graphite in a stream of He¹²). These results seem to indicate that in the course of gasification K_2SO_4 is reduced by H_2 or by CO to K_2S which is readily converted by steam to KOH. KOH was converted by CO, CO_2 or carbon to K_2CO_3 , and ultimately to K. Such sequential changes in the catalyst were supported by X-ray diffraction analysis of the K_2SO_4 - Al_2O_3 catalyst before and after gasification¹⁰). Thus, it is plausible that K_2SO_4 and K_2CO_3 operate in the same working state.

3.5 Gasification of Intermediate Carbon Deposited on Potassium Catalysts

It was shown previously that the reaction between carbon and potassium catalyst would be the key step in the gasification of graphite or char. To elucidate the gasification mechanism in the present case, especially the role of carbon deposited on K_2CO_3 , transient state experiments were carried out. The results are shown in **Fig. 8**. When Arabian Light atmospheric residue was fed to a fresh K_2CO_3 catalyst, both the total gas yield and $(\text{CO}+\text{CO}_2)$ yield initially increased and reached a steady state (I). After 3 hrs, the catalyst was flushed with CO_2 and the rate of CO formation was measured (II). The reaction between deposited carbon and CO_2 was very rapid at start and more than 80% of the deposited carbon was removed during the initial 30 min of run. After almost completely removal of the deposited carbon, gasification was repeated(III). The gas yield incre-

Reaction temperature : 900°C, Molar $\text{H}_2\text{O}/\text{C}$ ratio : 1.2, Feedstock : A/L atmospheric residue (72.0 g/hr), Catalyst : K_2CO_3 (K : 10 wt%) - Al_2O_3 (200 g)

Fig. 8 Variation of Catalytic Activity (I) and (III) and Variation of CO Formation Rate during the Removal of Deposited Carbon (II) with Time

○, ● : K_2CO_3 (17 g) on alumina (83 g) + activated carbon (50 g)
 □, ■ : K_2CO_3 (17 g) activated carbon (50 g) + alumina (83 g)
 Open symbol : 900°C, Closed symbol : 850°C ; Steam feed rate : 81.0 g/hr

Fig. 9 Comparison between Activity of K_2CO_3 and that of K_2CO_3 on Carbon

ased and attained the steady state equal to those of the experimental (I). The results strongly support the previous conclusions of the author that deposited carbon behave as an intermediate⁶).

Using the activated carbon specified in paragraph 2.1 as material similar to intermediate carbon, the subsequent studies were made. The activated carbon of 24–42 mesh particle size was mixed uniformly with the alumina-supported K_2CO_3 catalyst, and gasified under the conditions shown in Fig. 9. When carbon was completely gasified, another dose of carbon was charged to the fluidizing catalyst bed and the procedure was repeated several times with no catalyst make up. Fig. 9 gives the results with those of the reference experiments where a uniform mixture of activated carbon loaded K_2CO_3 and pure alumina was filled in the gasifier. Very rapid gasification was attained in both cases, and the variation in the rates of

CO and CO_2 formation completely overlapped. From these results, it is deduced that there is migration of a catalytically active component, probably gaseous potassium, between the catalyst and carbon particles. As the catalytic activity did not change at all in the gasification which was repeated several time, potassium had likely adhered to alumina surface.

To verify the migration of potassium between activated carbon and K_2CO_3 , the following experiments were carried out. 10–150 g K_2CO_3 (K:10 wt%) $\cdot \text{Al}_2\text{O}_3$ were mixed with 50 g activated carbon uniformly, and the gasification rates of the mixed materials were determined at 850°C. The results are shown in Fig. 10. With the 10 g $\text{K}_2\text{CO}_3 \cdot \text{Al}_2\text{O}_3$, the gasification rate was increased gradually with time, although it was slow at initial stage. After attaining the maximum value, the rate decreased very rapidly. On the other hand,

Reaction temperature : 850°C, Feedstock : Activated carbon 50 g,
Steam feed rate : 81.0 g/hr, Catalyst : K_2CO_3 (K : 10 wt%) - Al_2O_3

Fig. 10 Effect of Catalyst Loading on the Rate of C-H₂O Reaction

the rate curves in the figure were almost similar in the range 25–150 g. From the results, a small amount of K_2CO_3 would be sufficient to gasify the activated carbon. It seems that such a high activity of the catalyst at early stage depends on the rapid migration of potassium from K_2CO_3 to activated carbon, and that the potassium is in the gaseous state which is most easy to move. From the similar rate curves for 25–150 g catalysts, it seems reasonable to assume that the catalytically active component is metallic or ionic potassium and the amount of the migrated is restricted within the equilibrium value.

Fig. 11 shows the results of steam gasification of 50 g activated carbon mixed with 10 g K_2CO_3 - Al_2O_3 . At 30 min after the start, Ar was flushed to purge the steam completely. After purging, Ar was stopped, and steam was charged again. The procedure was repeated twice. The gasification rate of the activated carbon did not change before and after purging with Ar. Generally, the gasification rate increased with time, though the amount of activated carbon decreased. The result shows that the separated potassium migrates readily to the activated carbon and remains on its surface.

4. Discussion

Under the experimental conditions, there was no appreciable difference in catalytic activity among the various potassium compounds except KCl. A similar tendency was reported in the case of coal char¹¹⁾. It is reasonable to expect from the results of **Figs. 5, 6, 7** and **Table 2** that each compound undergoes thermal decomposition or reduction by

Reaction temperature : 850°C, Feedstock : Activated carbon 50 g, Steam feed rate : 81.0 g/hr, Catalyst : K_2CO_3 (K : 10 wt%) - Al_2O_3 10 g

Fig. 11 Comparison of Gasification Rate before and after Ar Flushing

H₂, CO, or C in the course of gasification. Each compound, after thermal decomposition or reduction, acts as a gasification catalyst. It is an important conclusion that the nature of anions is a minor factor in the catalysis by potassium species. Only KCl is difficult to decompose, and its anion appears to act as an inhibitor. From the results of these figures and **Fig. 4**, it is proved that the catalytically active component is not the potassium compound itself, but it is cationic or metallic potassium. Compared with CaO catalyst, potassium is an outstanding catalyst in the gasification not only of very heavy residues such as SDA residue but also of deposited carbon.

As already explained, K from K_2CO_3 migrates readily to the intermediate carbon, and stays on its surface. The gasification rate of the carbon with potassium is very fast.

Thus, a path of gasification of residual oils with

potassium compounds is proposed as follows :

(1) By thermal decomposition of the feed oils, the intermediate carbon formed deposits on the catalyst.

(2) K_2CO_3 on alumina is reduced to potassium by the reducing agents such as H_2 , hydrocarbons and intermediate carbonaceous materials from feed oils. The potassium migrates to the deposited carbon, and makes a complex. As author and co-workers have already reported, this step is the most important step, because the complex plays a valuable role in the gasification of carbonaceous materials.

(3) The complex(K-C) reacts with steam as follows.

Two ways are considered how steam reacts with the carbon. One is a direct attack of steam on the K-C complex. The other is explained by the so-called Langmuir-Hinshelwood mechanism, that is steam acts to the carbon through KOH. A reasonable answer to this problem is not yet given.

(4) The carbon in the K-C complex is easily consumed by the reaction with steam, and the remaining potassium makes a new K-C complex one after another until the feedstocks charging is stopped or the potassium is lost by some causes. The loss of potassium is mainly due to the reaction with ash. As the ash content of residual oils is very small in comparison with that of lignites,

the life of the catalyst used for the residual oils is far longer than that for lignites. Among the potassium compounds used in this study, the life of the potassium polyaluminate was the longest. This seems to indicate that the binding force between potassium cation and polyaluminate anion is somewhat stronger at the experimental temperature than that of the other compounds except KCl.

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要 旨

カリウム触媒による残油の水蒸気ガス化

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本論文は最近の著者の既発表論文に若干の未発表データを加えたもので、主としてカリウム系触媒による残油のガス化経路と活性を論じたものである。まず、残油の代表的なガス化触媒である石灰系触媒との比較、残油の C/H 比とガス収率の関係などから、カリ系触媒は特に重質な原料に有効なことを示し、次いで種々のカリウム化合物の活性の比較、触媒中の K 含量と活性の関係、熱天秤による K_2SO_4 の還元、 $\beta''\text{-Al}_2O_3$ の還元前後の X線分析結果などから触媒物質はカリウム化合物でな

く、K または K^+ であることを立証した。さらに経時変化と CO_2 導入の結果、活性炭と触媒およびアルミナ担体の種々の混合、活性炭への触媒添加量の影響などを検討し、触媒中の K は気体になって容易に析出炭素に移行し、一種の錯体を形成する。その錯体は水蒸気と反応して、炭素のガス化が起こり、後に K が残り、再び錯体をつくって順次ガス化を進めることなどを明らかにした。

Keywords

Catalytic gasification, Intermediate carbon, Potassium catalyst, Reaction path, Residual oil