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The basic study of methanol to gasoline in a pilot-scale fluidized bed reactor

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ABSTRACT

A fluidized bed reactor, used for methanol to gasoline (MTG), was designed followed the theory of gas–solid two-phase flow, and the effects of some factors, such as temperature, space velocity and the regeneration process, on the performance of MTG catalyst were systematically examined. The results show that: heat and mass transfer can be effectively conducted in the fluidized bed reactor; with the reaction temperature was increased, the methanol conversion rate maintained at 100% and the yield of gasoline gradually increased, then reached its highest value of 25.22% at 410 °C, after that it began to decline; and the C_5 aromatics content increased with temperature and reached its maximum value of 49.86% at 430 °C. With the weight space velocity was increased, the yield of gasoline firstly increased and then decreased, while the C_5 aromatics content was decreased; In addition, the effect of inner-regenerated process for used catalyst is very good. Low temperature can help to generate lighter olefin polymer, the higher extent of hydrogen transfer and cracking of large molecules at middle temperature, the carbon deposition reaction and aromatization reaction of low carbon olefin occurred at higher temperature, all of these contributed the above mentioned rules. While the weight space velocity acts on the performance of catalyst mainly via influencing the contact time and the carbon deposition reaction.

1. Introduction

China is a fast developing country and is also the second energy consumption country just after the US in the world, but China has poor petroleum reserves. Petroleum supply has been relying more heavily on import. It is estimated that the consumption of crude oil in China will reach 450–610 Mt tons by 2020, of which 60–70% need to be imported [1]. This will have a negative effect on China's economic-social development and energy security strategy. Therefore, it is necessary to develop a fuel-produced technology which can produce alternative petroleum in a larger scale [2–4].

Biomass, natural gas and coal can be used to produce alternative petroleum [4–6]. But the feedstock of biomass was usually heavily affected by season, years or producing sites, and biomass usually has a relatively larger distributing area comparing with its total amount [3]. So it is inefficient in collection and pretreatment of biomass-based feedstock. In addition, the bio-oil production process is complicated and inefficient [7], and the poor quality and expensive purification process which usually related with the produced bio-oil [7–10]. All of these limit the utilization of biomass as feedstock [11,12]. While natural gas resource in China is deficient, and synthetic natural gas (SNG) from coal has being developed by some Chinese corporations. So the development of natural gas-based oil is not feasible in China [13,14]. On the other hand, China has abundant coal resources. So the production of coal-based liquid fuel to alleviate the petroleum importation has been paid more and more attention.

Direct and indirect liquefaction of coal are two routes for producing coal-based liquid fuel. The latter firstly converts coal to syngas [15], and the syngas is used to produce hydrocarbon fuel by Fischer–Tropsch (FT) systems, or to produce methanol, and then convert methanol to gasoline (MTG) or diesel (MTD) [16]. Among which, the MTG process has the following advantages: technology is relatively simple, can help to relieve some of the methanol oversupply and obtain high-octane gasoline. Especially, when other carbonaceous materials such as biomass, black liquor (from industrial paper manufacture), coke oven gas or natural gas are used to produce syngas and methanol, and then the methanol is converted to gasoline by MTG. By this the problems mentioned in the introduction and encountered during utilization of biomass can be avoids and provides a useful method for producing gasoline with less technical risk. And thus MTG is becoming a promising

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technology in China [17,18]. While the developments of processes and catalysts with high performance are very important for successfully running a MTG plant [19]. At present, an industrial fixed bed MTG unit has been successfully operated by Mobile Company [16,20]. However, the disadvantages of poor heat and mass transfer for fixed bed limit the further development of this technology. On the other hand, fluidized bed has been worldwide used in many industrial areas [21–23], and this technology has the advantages of good heat transfer, perfect temperature distribution, and low investment. All of these have provided an ideal condition for MTG catalyst. But the feasibility of fluidized bed methanol to gasoline technology (FMTG) has not been validated. In addition, the catalyst that can be used in fluidized bed also needs further research, while these are indispensable for the design, operation and scale-up the industrial FMTG. In other words, the lacks of these researches have limited the development of the FMTG.

In order to solve the above problems, a pilot-scale fluidized bed MTG apparatus with inside diameter of 100 mm and height of 4000 mm was designed and constructed. This pilot-scale fluidized bed MTG apparatus was designed based on the results of cold-state experiment, the gas–solid flow parameters and the reactive characteristics of MTG process. Some basic hot tests have been carried out on this apparatus, and the stability of fluidized bed MTG apparatus, the heat exchange capability and its ability of gas–solid separation were systematically studied. In addition, the effects of temperature and space velocity on the performance of catalyst were also investigated in this paper. All of these results can help us to design, operate and scale-up the industrial FMTG process.

2. Experimental

2.1. Catalyst preparation

A special ZSM-5 molecular sieve was used as main active element and silicon aluminum glue as binder, and compacted catalyst was produced via an extrusion process and then it was calcined for 3 h at 550 °C. Finally, some auxiliary agents were added and catalyst for MTG was obtained, the obtained catalyst was denoted as ZSM-5-80. Its size distribution, surface area and average particle size were shown in Fig. 1 and Table 1. From which it could be seen that the particle sizes of the catalyst are between 10 and 100 μm and behave as normal distribution, its volume average particle size is 62.76 μm. These characters of the particle size can guarantee the successful separation of the catalyst from the mixture of product and catalyst. The critical fluidization velocity of catalyst is 0.0023 m/s and carrying velocity is 0.135 m/s. The BET surface area of catalyst is 323.83 m^2/g. This surface area can provide larger contact area between catalyst and reactant, and thus increase the contact time between them. While the special pore structure and surface properties can help the catalyst to prefer adsorb reactant, namely methanol, to the surface of catalyst and then the adsorbed methanol enters the inner cavity of catalyst. This can make the reactions to process toward the direction of gasoline production. Thus increasing the depth of reaction and maximizing the yield of gasoline.

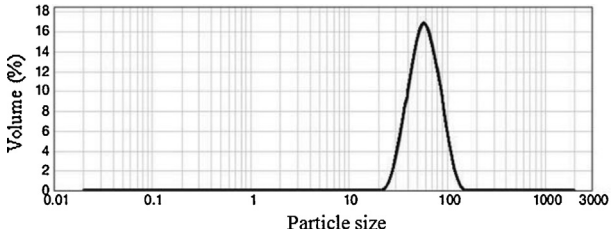

Fig. 1. The size distribution of the catalyst used in the fluidized bed apparatus for methanol to gasoline in a pilot scale.

Table 1
Surface area and average particles size of catalyst used in the fluidized bed apparatus for methanol to gasoline in a pilot scale.

Spacing diameter (μm)	BET surface area (m^2/g)	Surface area average particle diameter (μm)	Volume average particle diameter (μm)
0.93	323.83	55.82	62.76

2.2. Hot test apparatus and processes

All experiments were conducted in a fluidized bed apparatus, the schematic diagram of fluidized bed apparatus for methanol to gasoline is shown in Fig. 2. In this figure, R001 is the fluidized bed reactor with inside diameter of 100 mm and height of 4000 mm. According to the critical fluidization velocity and carrying velocity, the gas velocity is chosen as 0.12 m/s and bed height is about 1.14 m. The processing capability for methanol is 2 kg/h and as much as 4 kg catalyst can be lauded. The lower part of the fluidized bed is the main space for converting the methanol. So the R001 is further divided into four stages from bottom to up. The stage 1 belongs to the zone of dense phase, where the reaction rate of MTG is the fastest, and thus its temperature also is the highest (435–468 °C); the stages 2 and 3 belongs to the zone of dilute phase, and where the reaction temperature is moderate, slightly lower than 1; while the stage 4 belongs to the zone of free, where almost no reaction occurs. Table 2 shows the typical temperature values of different stages during long-termed operation of this device. From this table it could be seen that a uniform temperature distribution is obtained in the inner of the fluidized bed reactor, reflecting its perfect heat and mass transfer ability.

The typical reaction conditions of MTG experiment are shown as following: temperature: 380–450 °C; regenerated temperature: 500–600 °C. The experimental procedure is described as follows: the catalyst was added from the feed port which was mounted in the upper of reactor. Methanol from methanol metering pump is pumped into the methanol preheater, preheated to 120 °C and vaporized as methanol vapor, and then the methanol vapor is entered into the fluidized bed reactor, contacts with the previously added catalyst and reacts. The gas products and the entrained catalyst enter into the cyclone for gas–solid separation. After that the separated catalyst outflows from the lower portion of the cyclone and is collected in the collecting tank. The separated gas passes through the metal filters and enters into the heat exchanger to cool as condensate. The condensate flows into the liquid product storage tank, and the non-condensable gas is sampled and vented through a gas flowmeter. The fluidized bed apparatus and its auxiliary system can steadily and efficiently runs.

Table 2
The temperatures of different stages in the fluidized bed reactor during its long-period running.

Run number	Temperature of stage 1 (°C)	Temperature of stage 2 (°C)	Temperature of stage 3 (°C)	Temperature of stage 4 (°C)
1	466	453	435	410
2	468	457	436	417
3	468	457	437	414
4	467	454	434	414
5	455	439	432	417
6	439	425	434	431