유동층 반응기를 이용한 Chlorodifluoromethane 열분해

김형천, 김희영, 우성일*
한국화학연구소 화학공학연구부, *한국과학기술원 화학공학과

Pyrolysis of Chlorodifluoromethane in a Fluidized Bed Reactor

Hyung Chun Kim, Hee Young Kim and Seong Ihl Woo*
Department of Chemical Engineering, Korea Research Institute of Chemical Technology (KRICT), *Department of Chemical Engineering, Korea Advanced Institute of Science & Technology (KAIST)

Introduction

Ultrapyrolysis or ultrarapid thermal pyrolysis is characteristic of high reaction temperature above 700°C and short reactant residence time much less than 0.5 s. The extreme nature of ultrapyrolysis requires new reactor systems corresponding to a feedstock and desirable products. In designing a new reactor system, the most critical and basic element to be considered is how to supply heat required for the reaction. The present research deals with an application of microwave heating for the ultrapyrolysis process with the pyrolysis of chlorodifluoromethane ($CHClF_2$; R22) as a representative reaction for testing the proposed heating method. The primary product of the reaction is tetrafluoroethylene (C_2F_4; TFE) used as monomer for Teflon. Following kinetic studies for R22 pyrolysis by many workers [1-5], the R22 pyrolysis can be classified as a case of ultrapyrolysis: a reactor system to be used must be able to heat rapidly the reactant (R22) to temperatures of 700~800°C; to supply the reaction heat as high as 30 kcal/mol; and then to quench the product gases to less than 400°C immediately after a residence time of 30 to 500 milliseconds. Conventional fluidized bed reactors have been considered not to be efficient for the ultrapyrolysis process. Thus, tubular reactor systems have been widely used for the R22 pyrolysis with superheated steam as a major heating medium. The present study presents that a fluidized bed reactor heated by microwave can be a recommendable means with high heat transfer rate required for ultrapyrolysis. Furthermore, the performance of R22 pyrolysis in the reactor will also be studied.

Experimental section

A schematic drawing of an experimental apparatus is shown in Figure 1. A quartz tube (ϕ45x478 mm) was used as a reactor, and the tube was insulated with Kaowool®. Particles of active carbon (average d_p: 0.34 mm) were selected as a fluidizing heat carrier satisfying both high absorption of microwave and inertness to reaction. They were loaded to the height, on packed basis, 180 mm from a gas distribution plate made of sintered metal. R22 (GENETRON-22, Allied Co.) was supplied into the upper side

of the fluidized bed through a nozzle tube (1/4 in.). This tube was inserted from the top-side of the reactor and was allowed to be adjusted according to predetermined height of its outlet. The R22 fed was mixed with nitrogen gas that was used as fluidizing gas and supplied through the distributor plate. There was no preheating of both R22 and nitrogen gas before feeding. Thus, the pyrolysis reaction was arranged to proceed at the upper side of the fluidized bed, while its lower side below the R22 nozzle outlet was utilized as a heating zone for the generation of heat by microwaves. The gas exiting from the reactor was immediately cooled by a cooler. Microwave from a generator (JRC Japan; 2,450 MHz, 5 KW) was introduced into the lower section of the fluidized bed for heating the fluidizing particles. Temperatures in the bed were measured with sheathed-thermocouple (1/4-in, multi-point), and were regulated by adjusting the microwave generator. Analysis of product gases was executed by an on-line gas chromatograph (GC) with Carbopack B/5% Fluorcol® column (Supelco, Inc).

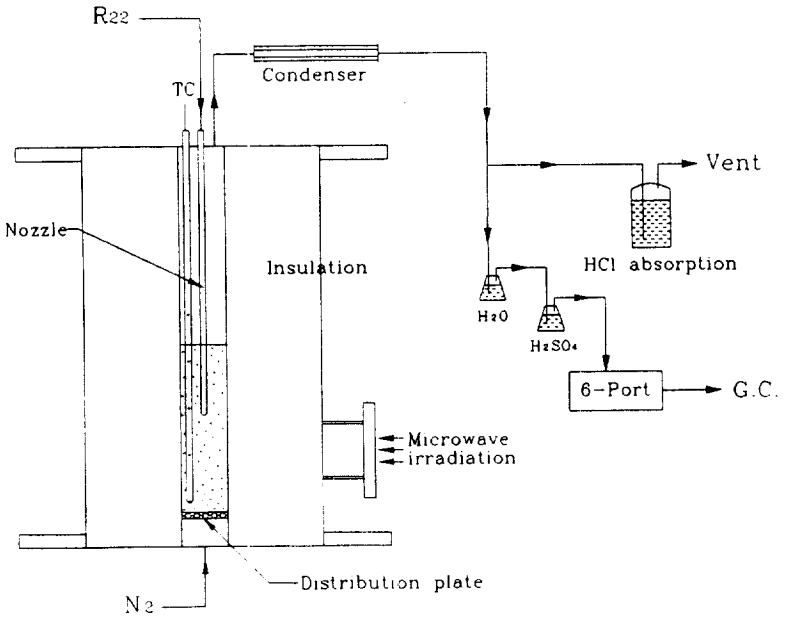

Figure 1. Schematic diagram of R22 pyrolysis apparatus

Experimental results and discussion

Heat supply : Although microwave was locally irradiated to the solid particles in the heating zone of the fluidized bed, the temperature difference between the heating zone and reaction zone was less than 2°C when the bed temperature was controlled at 750°C. Also, right after R22 was fed into the bed at a rate of 0.12 mol/min, any noticeable decrease of its temperature was not observed in spite of heat consumption by endothermic R22 pyrolysis. These observations support that the internal heat

transfer of the fluidized bed is fast enough for the heat required to be transferred from the heating zone to the reaction zone. It is clear that the major heat-transfer resistance imposed by the reactor walls could be eliminated by the direct irradiation of microwave into the fluidized bed. In addition, the fraction used for R22 pyrolysis among the microwave energy supplied was as high as 70~80 %.

R22 pyrolysis in a fluidized bed: Variables considered in experiment were reaction temperature, residence time, the velocity of fluidizing gas, and R22 feed rate. Figure 2 presents the effect of temperature on reaction, using residence time as a parameter. The formation of TFE began to be detected at about 600°C. Increasing temperature above 600°C resulted in the increase of conversion and the decrease of selectivity. TFE yield, expressed as multiplying conversion by selectivity, increased with temperature since the increase of the conversion was more prominent than the decrease of the selectivity. However, further increase of temperature above 740°C revealed the rapid decrease of the selectivity due to serious formation of side products, which resulted in the decrease of yield. The observations shown in Figure 3 reveal that TFE yield is not sensitive to residence time at the range tested. The slight increase of the conversion with residence time was offset by the slight decrease of selectivity. However, at the longer residence time over the tested range (> 0.3 s), the decrease of selectivity is expected to overwhelm the increase of conversion, causing the resultant value of yield to decrease. The effect of the fluidizing gas velocity on TFE yield is presented in Figure 4. Over the range of fluidizing gas velocity, 15~33 cm/s, TFE yield increases gradually as the fluidzing gas velocity rises. This was mainly attributed to the enhancement of TFE selectivity, while the conversion was not influenced by the change of fluidizing gas velocity. Although the increased velocity of fluidizing gas should benefit the conversion by the improved heat transfer rate, this effect might be adversely offset by the increase of diluent ratio and by the decrease in residence time. The increase of diluent ratio would suppressed side reactions characteristic of bi-molecule reaction. As a result, the TFE selectivity increased, while the conversion remained constant irrespective of the change of velocity of fluidizing gas. The effect of the variation of R22 feeding rate on TFE yield is illustrated in Figure 5, which shows almost a constant value of TFE yield, except for the case when R22 feed rate is less than 0.06 mol/min. The range of the feed rates tested correspond to the dilution ratios over 1.9~20. It is conceivable that the temperature effect on the performance of R22 pyrolysis was so large that the dilution effect becomes negligible at low degree of dilution. However, the high TFE yield was observed when R22 feed rate is small (dilution ratio > 10). This result can be described by the reason that the effect of dilution on selectivity becomes pronounced and the side reactions are suppressed if R22 is diluted highly. As a whole, the microwave heating method enabled the conventional-type fluidized bed reactor to be utilized for the ultrapyrolysis process. High TFE yield more than 60% could be obtained under the proposed fluidized bed reactor even without sufficient optimizations for reactor design and operation conditions. The output is comparable to the commercial values based on tubular reactor systems that use superheated steam (~1,000°C) as a major heat source for the highly endothermic reaction.

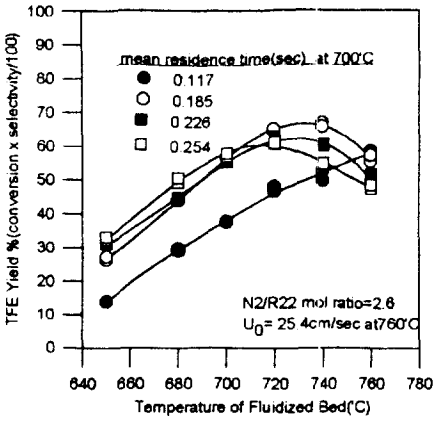

Figure 2. The Effect of Temperature on TFE Yield

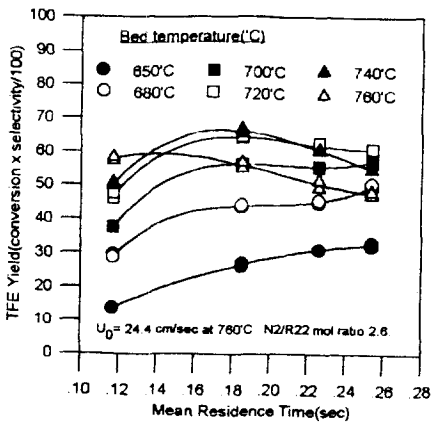

Figure 3. The Effect of Time on TFE Yield

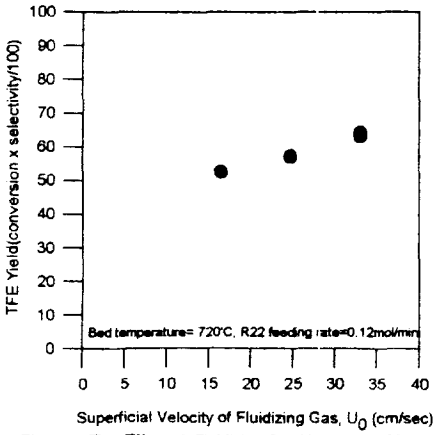

Figure 4. The Effect of Fluidizing Gas Velocity on TFE Yield

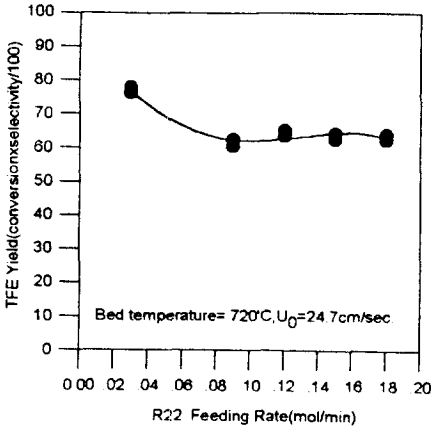

Figure 5. The Effect of R22 Feeding Rate on TFE Yield

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