

CHAPTER I

INTRODUCTION



1.1 Background

In propylene process industry, contaminated in propylene product, acidic components, such as hydrogen sulfide (H_2S), carbonyl sulfide (COS), carbon monoxide (CO), and carbon dioxide (CO_2), were either directly contaminated from raw materials or intentionally formed by side reactions of various impurities in raw materials namely propane for dehydrogenation process or ethane/propane, naphtha, and atmospheric gas oil for thermal cracking process. These impurities become serious problems strictly concerned by down-stream manufacturers.

Ordinarily, sulfur compounds contaminated in petroleum hydrocarbons because it is a sulfur source and a potential atmospheric pollutant, causing air pollution and corrosion. Particularly, the impurities with electron donating group i.e., CO, H_2S , COS and mercaptans have a direct effect on Ziegler-Natta catalyst and metallocene catalyst, the well-known catalysts for polypropylene process industry. These compounds are inhibitors and poisons. On the other hand they can adsorb to the active sites and react with the catalysts, causing deactivation or decomposition of the catalyst complex. Furthermore, trace quantity of reactive sulfur compounds is poisonous to hydrocracking catalyst, reforming catalyst, including many purification catalysts. Consequently, the removal unit of reactive sulfur compounds should be placed up-stream of any other purification units (see appendix A).

The most reactive sulfur compound in the impurities of propylene, carbonyl sulfide, is necessary to be minimized or extinguished from propylene if feasible particularly polymer grade. COS level in some polypropylene feedstocks may range from an acceptable level of < 50 ppb to totally unacceptable levels of over 2 ppm or not over 20 ppb for BASF propylene specification (see appendix B). Carbonyl sulfide is an undesirable impurity in petroleum hydrocarbon and has been found to be one of the most troublesome impurities. It may not be merely directly introduced into the

process as a contamination that conventionally presented in the raw materials but also formed in the treating process due to the molecular sieve-catalyzed reaction of carbon dioxide with hydrogen sulfide or other sulfur compounds, such as the reaction shown below.



In the past, a solid NaOH bed has been used commercially, but NaOH alone is not capable commercially of lowering the COS concentration to < 50 ppb.

The separation of COS by processes which involve distillation, in addition, are extremely cost due to the cost of energy to vaporize virtually all of the liquid. It is, therefore, desirable to provide other means for the removal of COS impurities from organic liquids. Unfortunately, for the purification process of hydrocarbons especially propylene production, the boiling point of propylene (-48°C) and one of COS (-50°C) are so closed. Consequently, in the range of a few parts per million, concentration of COS are very difficult to separate from propylene by fractional distillation. Also, COS is not completely removed from propylene by the usual sulfur-removal processes such as caustic scrubbing or amine-type scrubbing.

Hereupon, COS removal appears dominant to develop on the basis of high efficiency, mild condition and low cost.

In order to convert COS to H₂S, hydrodesulfurization using Co/Al₂O₃ catalyst at 673-1073 K obtained 87.5% conversion that is high efficiency but high severity (1). One of the mild condition process of COS removal was the absorption onto liquid amine compounds at temperature 283 to 333 K. The kinetics of this reaction was found to be determined entirely by the zwitterion protonation rate. Nevertheless, there were many kinds of products from reaction amine derivatives, that should be removed by further process (2). Consequently, adsorption, the popular and practical technique has many advantages for removal of trace contaminants in hydrocarbons such as highly efficiency, massive capacity, low cost of investment. BASF R3-12[®] catalyst, CuO and ZnO on alumina, has been applied in many factories used BASF

know-how in order to remove COS in propylene; nonetheless, the 400°C operating temperature is quite high. It is known to hydrolyze COS over a platinum sulfide/alumina catalyst, such catalysts have not been used for the hydrolysis of small amounts of COS in propylene possibly. The operating conditions are mild, but the cost of the catalyst so expensive.

The new generation of selective adsorbent, Alcoa Selexsorb®COS, which comprises an activated alumina adsorbent impregnated with proprietary modifiers, (alkali metal or alkaline earth metal or mixture of any two- or more of such compound) has been used for COS removal in hydrocarbons like propylene. The outstanding advantages of this selective adsorbent are the high efficiency and the adsorption process of liquid hydrocarbons at ambient temperature, even temperatures of from 15 to 100°C.

There was only study of the capacity of this selective adsorbent including the proper quantities alkali metal or alkali earth metal (3). In a consequence, the kinetics of adsorption of COS on Selexsorb®COS would, therefore, be substantially fascinating to study and expect to obtain the kinetics equation for various models.

1.2 Aim and Research Strategies

In order to know the elementary kinetics of adsorption of carbonyl sulfide on Selexsorb®COS, the monitoring of COS amount that left after continuous reaction by means of gas chromatography equipped with pulse flame photometric detector, will be calculated initial reaction rate, rate constant, the order of reaction, the frequency factor, and the activation energy. There are two parameter studies which are the operating temperature, and the quantity of initial carbonyl sulfide. The data of kinetics obtained from this study may be applied for some operating systems either batch process or continuous process.

Furthermore, the kinetics parameters of COS adsorption on Selexsorb COS become important data to follow the efficiency of adsorption, the period of the adsorbent regeneration as well as life time of the adsorbent.

On the ground of very low concentration of carbonyl sulfide left after reaction, the determination of COS lower than detection limit of the detector is highly required in order to gain high accuracy and precision. The appropriate condition of analysis using the gas chromatograph equipped with pulse flame photometric detector (GC-PFPD) with lower detection limit of 20 ppb or less, was accorded to the optimum flow of carrier gas (nitrogen), hydrogen, and air; the optimum temperature of injector, column oven and detector as well as voltage of photomultiplier tube (4). Moreover, the selection of proper type of column is very significant to improve sensitivity.

Concerning initial reaction rate, the order of reaction, rate constant, the activation energy as well as the rate equation, both the variation of carbonyl sulfide (reactant) concentration and the variation of reaction temperature, at the proper ratio of amount of adsorbent to volume of reactor that was previously tested, were studied in various flow rate of reactant so that the adsorbed COS amount of the reaction rate at steady state was obtained. Ultimately the kinetic parameters were fit in the Langmuir model with the assumptions for the elementary kinetics.

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