Synthesis of P-xylene by selective methylation of toluene

Abstract - Para-xylene (or p-xylene) is an industrially significant compound which is used to synthesize terephthalic acid used for the production of poly-ethene terephthalate (PET). It is also used to manufacture shrink films and magnetic tapes. The proposed flowsheet was specifically designed for the production of p-xylene by considering catalysts which showed high selectivity for it, such as H-ZSM-5. In this study, the process of production of p-xylene by the selective methylation of toluene was simulated using DWSIM open source chemical process simulator. The NRTL property package was chosen as the basis for simulating the entire process. A plug flow reactor was used to execute the synthesis of p-xylene. In this process, along with the desired product, methanol of high purity was also produced. The feed was chosen (based on sensitivity analysis) to produce 20 tonnes/hour (1 US tonne = 907.185 kg) of p-xylene. The effect of reactor volume and length were also studied.

Keywords—p-xylene, Methylation, Plug flow reactor, Selectivity, Sensitivity analysis.

INTRODUCTION:

Para-xylene is one of the three isomers of xylene. Its structure consists of a methyl group attached to the para position of a benzene ring. P-xylene can be synthesized by the catalytic reforming of naphtha. After the separation of xylene from aromatics, the p-xylene isomer has to be separated from the other isomers of xylene by using crystallization or adsorption. Since all the xylene isomers have very close boiling points, the separation of p-xylene from the xylene mixture becomes difficult and requires a lot of energy. Thus, an efficient and cost effective process must be adopted. One such alternative for the production of p-xylene is by methylation of toluene. Methylation of toluene is done by the reaction of toluene and methanol over a zeolite catalyst, such as ZSM-5, to yield water and xylene products. The other isomers do not have much industrial demand and they have to be converted to p-xylene by isomerization.The catalyst employed during the methylation of toluene is **H-ZSM-5**, which upon modification of pore size shows high selectivity towards the formation of p-xylene.

The rate equation for the reaction of toluene with methanol is given as:

$$\mathbf{r = k\,[Toluene][Methanol]}$$

The reaction kinetics is as follows: **Pre-exponential factor, A = 408 mol/(g.h.atm)**

Activation energy, Ea = 46.1 kJ/mol

MASS FLOW OF VARIOUS STREAMS IN (kg/hr)

Compounds	Feed	Reactor outlet	Distill top	Distill bottom
Toluene	17400	6.518×10^{-20}	1.86×10^{-20}	4.5×10^{-20}
Methanol	12613.33	6562.48	6552.50	8.49
P-xylene	0	20048.648	1015.62	19037.12
Water	0	3401.97	1447.70	1954.38

FLOWSHEET DESCRIPTION:

The production of p-xylene by methylation of toluene was simulated using the DWSIM open source software. In this process simulation, the reactants, namely, toluene and methanol which were initially at 25◦C and 1 bar, were pumped into a heater with a pressure of 3 bar. The reactants were heated to a temperature of 400◦C and fed to the mixer. The mixer outlet was then fed to the plug flow reactor. This reactor was considered to have a volume of 60 cubic meter and length of 1 meter. The reaction was assumed to be irreversible and the values of activation energy and Arrhenius factor used were 46.1 kJ/kg and 408 mol/(g.h.atm), respectively. The product from the plug flow reactor outlet was in vapour phase at 400◦C. It was then cooled to 50◦C using a cooler. The product from the cooler outlet was fed into the rigorous distillation column in which the top stream consisted of methanol and water, while the bottom stream consisted of water and p-xylene. Since water and p-xylene are immiscible and form different phases, they were separated using a decanter. In the flowsheet created, a compound separator was used as a decanter due to the lack of a more specific unit operation model on DWSIM.

RESULTS AND DISCUSSION:

For the plug flow reactor in which the reaction takes place, sensitivity analysis was done by varying the reactor volume and reactor length and noting its effect on the mass flow of para xylene in the reactor outlet. The effect of residence time on the reactor volume was analyzed by varying the reactor length and keeping the diameter constant. Since the length of the reactor is increasing, the residence time (time taken by the reactants to cover the reactor length) also increases. Thus, from the plot shown in Fig.3 it can be inferred that the reactor volume increases as the residence time increases.

The effect of reactor length on the pressure drop was also analyzed. From Fig. 4 it was observed that the pressure drop increased as the length increased. When the length of the reactor is increased, the reactants have to travel a longer distance, resulting in the increase in pressure drop. Since the kinetics of the reaction is dependant only on the temperature and concentration, change in any other factor such as reactor volume or length will not effect the product formation. This is because, hydrodynamic factors (such as pressure drop) vary proportionately so as to compensate for changes in volume.