

Effects of Different Processing Parameters on Divinylbenzene (DVB) Production Rate

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Abstract

The effect of processing parameters such as temperature, steam injection rate, and inert carrier gas flow rate on DVB and ethyl vinyl benzene (EVB) production rate was investigated and discussed in isothermal condition and atmospheric pressure in an experimental scale packed bed reactor. The results show that the temperature increases the DVB production rate significantly.

Keywords: Diethylbenzene (DEB); divinylbenzene (DVB); processing parameters; production rate.

1. Introduction

DVB is a very important chemical which is used as crosslinking agent in polymer industries. DVB as an intermediate is used for production of other chemicals. DVB can be produced by catalytic dehydrogenation of diethylbenzene (DEB) at different temperatures and atmospheric pressure. The reaction is endothermic and equilibrium limited. The byproducts of the DVB consist of a mixture of various gases and liquids. The desired products are DVB and EVB. Steam is used in this system for various purposes which will be explained later. Therefore, in this paper we discuss the effect of various processing parameters on the production rate of these two main products. A few papers in the literature directly address the preparation of DVB [1-3]. Various catalytic systems have been introduced in the literature for DVB production [1]. Iron based catalysts are used in experimental and commercial scale for DVB production. Different techniques such as simple mixing of catalyst ingredients followed by calcinations, sol-gel method for supported catalysts and co-precipitation method in industrial scale are used for catalyst preparation. EVB is produced simultaneously with DVB. Separation of EVB is not necessary and mixture of DVB and EVB is used in industrial scale for the production of polystyrene ion exchange resin beads. There are several facts about dehydrogenation reactions that should be known:

- 1 - Dehydrogenation is an endothermic reaction, thus, the equilibrium conversion and reaction rate increases at high temperatures. Also at low pressures, the conversion is high because the product volume exceeds the reactant volume.
- 2 - Gas phase dehydrogenation reaction rate increases with increase in partial pressure of reactants.
- 3 - Removal of hydrogen from products shifts equilibrium and reaction rate to high conversions.
- 4 - Dehydrogenation catalysts are less sensitive to poison due to reversible adsorption at high temperatures.

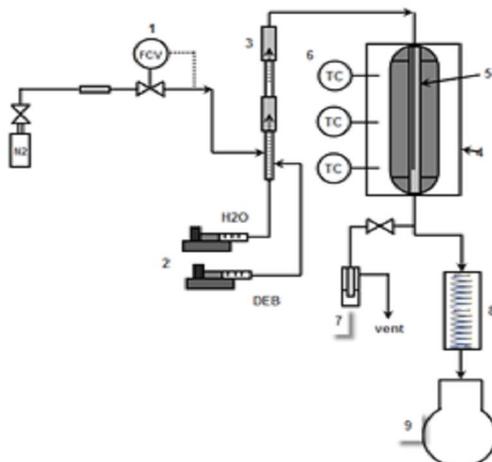
Endothermicity, low pressure and high temperature with the existence of competitive reactions make the designing of economical and efficient dehydrogenation process difficult. Catalytic dehydrogenation reaction is a complex phenomenon and understanding its mechanisms and kinetics is difficult. A packed bed reactor is used for DEB dehydrogenation to DVB. Various pseudo-homogeneous and heterogeneous models are used for catalytic process simulation. Depending on the complexity of the model, various parameters are considered in the mathematical modeling of these processes. The continuum model is more popular due to simplicity in manipulation the mathematical equations. In these models, the temperature and concentration gradients in the catalyst pellet are ignored. Various processing parameters affect the selectivity and conversion of DVB. In this study, we investigated the effects of processing parameters on DVB production rate experimentally.

2. Methods

An integral reactor with effective length of 30 cm and 1 cm diameter was used for the preparation of DVB. DVB was produced at different processing conditions. Two syringe pumps were used to inject water and DEB to the

evaporator at desired flow rates. An electric furnace was used to keep the temperature constant during the reaction.

Figure 1: Schematic diagram of the set-up. The elements of the set-up: 1-gas flow meter, 2-syrenge pumps, 3-preheater, 4-furnace, 5-reactor, 6-temperature controller, 7-scrubber, 8-condenser and 9-reservoir.



The schematic diagram of the set-up is shown in Figure 1. Before entering to the reactor, a preheater was used to heat up the steam and DEB. The liquid products were analyzed by GC-mass analyzer. The solvent which is used in GC-analyzer was dichloromethane. GC-mass analyzer spectra can be seen in Figure 2 for liquid products at 620 °C. A list of various liquid products, peak area and retention time, which was obtained by analysis of Figure 2, is shown in Table 1.

Figure 2: GC-mass result for the liquid products at 620°C.

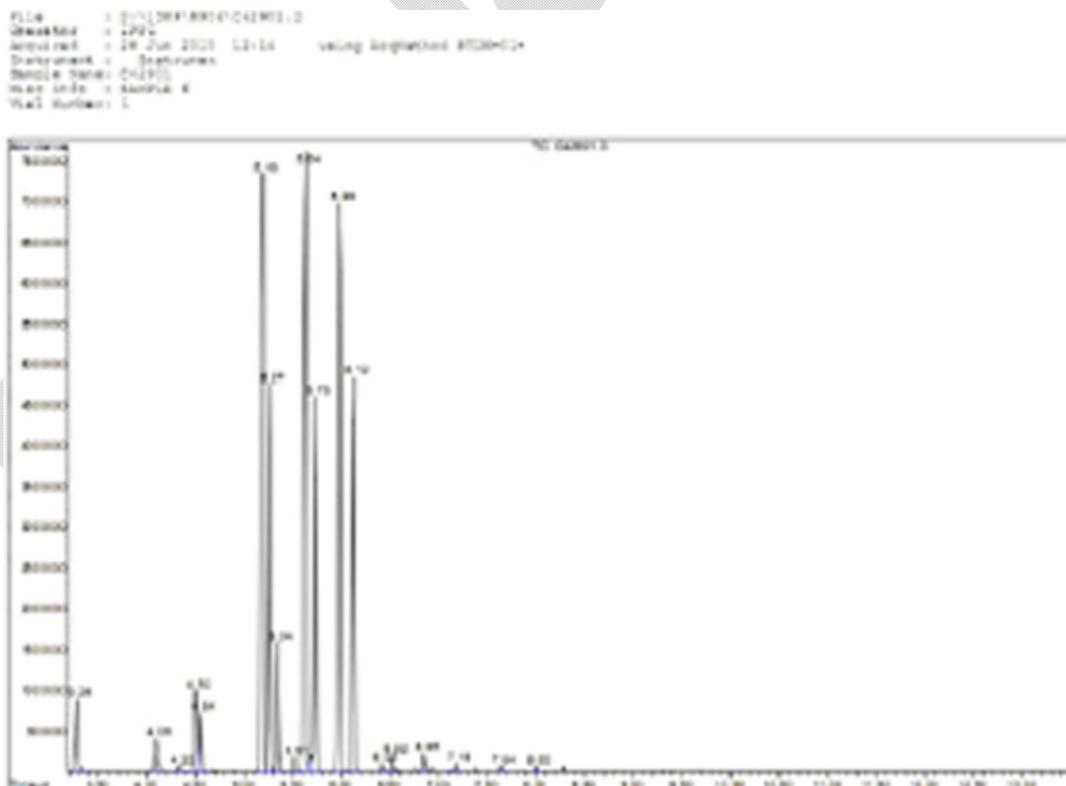


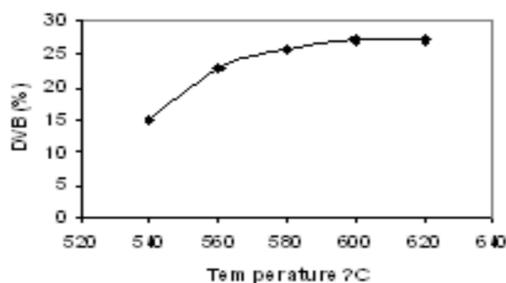
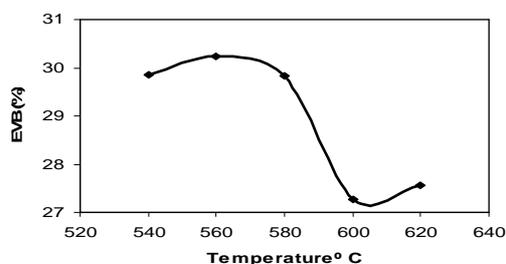
Table 1: GC-mass analysis for the liquid products.

Substance	RT	Wt (%)	Substance	RT	Wt (%)
Benzene	1.84	0.76	DEB	5.22	29.50
Toluene	2.27	1.19	EVB	5.70	28
Ethylbenzene	3.01	0.86	DVB	6.05	28.11
Xylene	3.08	0.48	Ethenyl-methyl-benzene	4.59	3.62
Styrene	3.32	2.67	Ethyl-methyl-benzene	4.13	2.11

3. Results and Discussion

3.1. Effect of temperature

Figures 3 and 4 present the effect of temperature on DVB and EVB conversion. As it is seen the DVB conversion increases with increasing temperature. Actually, the dehydrogenation of DEB to DVB is a two steps process. Initially DEB is dehydrogenated to EVB and then EVB is dehydrogenated to DVB. There is a possibility for DEB to be dehydrogenated to DVB directly. At 540 °C the conversion is 15% while the conversion at 620 °C is 27%. Therefore, 80 °C increase in temperature increases the conversion significantly. At lower temperatures the effect of is high, but at temperatures between 580 °C to 620 °C the effect is low. Comparison of the conversion at 600 °C and 620 °C shows that there is no significant change in conversion when we increase the temperature from 600 °C to 620 °C. Therefore, it can be concluded that the optimum temperature for the production of DVB is below 620 °C and close to 600 °C. The shape of production rate curve of EVB is completely different in comparison with DVB. Initially the production rate increases with temperature up to 560 °C and then reduces sharply up to 600 °C and again increases. The extent of the effect of temperature on production rate depends on the reaction rate constants. Decrease in production rate of EVB with temperature does not mean that the reaction rate is decreasing with temperature; it can be due to fast consumption of EVB to produce DVB. Dehydrogenation of DEB to EVB and DVB is in competition with the dehydrogenation of EVB to DVB. Depending on the sensitivity of the reaction rate constants to temperature and equilibrium constants the reactions will proceed with temperature. The reaction rate constants and equilibrium constants have not been given as a function of temperature.

**Figure 3:** Effect of temperature on DVB production rate.**Figure 4:** Effect of temperature on EVB production rate.

3.2. Effect of steam to DEB ratio

Steam is used in the DVB production. Steam has following advantages in DVB production:

- 1-It shifts the equilibrium towards higher DVB production by lowering the partial pressure of the products.
- 2-It supplies part of the heat is required for the endothermic reaction.
- 3-It prevents catalyst over reduction and deactivation by controlling the valence state of iron i.e. prevent reduction to metallic state and limiting it to Fe_3O_4 under reaction conditions.
- 4-It prevents coke formation on the surface and pores of the catalyst by reacting with the coke at high temperature.

At constant DEB injection rate of 16.7 cc/hr and 620 °C temperature the effect of steam injection rate on the overall production rate of DVB and EVB was investigated. The effect of steam injection rate on the EVB and DVB production rate is presented in Figures 5 and 6. Figure 5 presents that the production rate of DVB has a minimum at around 8 cc/hr steam injection. After this point, the production rate increases up to 40 cc/hr and then decreases. Highest production rate of DVB is achieved at 40 cc/hr of steam injection. The steam to DEB volume ratio at this point is 2.4. Comparison of Figures 5 and 6 shows that when the production rate of DVB is low the production rate of EVB is high (see point 8 cc/hr) and when the production rate of DVB is increasing the production rate of EVB is decreasing (see rest of the curves in Figures 5 and 6). It can be concluded that the increase in steam injection rate increases production rate of DVB (dehydrogenation of EVB to DVB) significantly. The effect of steam injection rate on EVB and DVB production rate is not similar. Both reactions are dehydrogenation but the effect on EVB dehydrogenation leading to DVB is significant. Therefore, to achieve highest production rate for DVB the steam to DEB volume ratio should be around 2.4. It must be noted that the volume ratio is in liquid state of DEB and steam. DVB is produced from dehydrogenation of DEB and EVB simultaneously. It is seen that with increasing steam injection rate both dehydrogenation reactions is facilitated. DVB has two unsaturated bonds and can establish two bonds for crosslinking, therefore is the desired product.

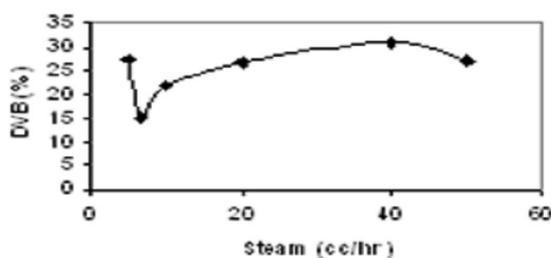


Figure 5: Effect of steam injection rate on DVB production rate.

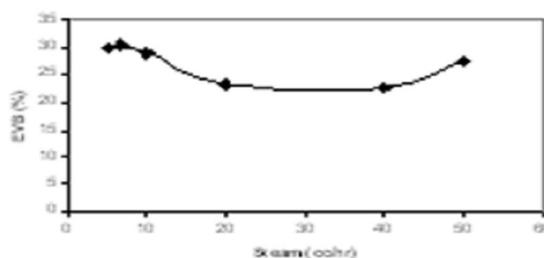


Figure 6: Effect of steam injection rate on EVB production rate.

3.3. Effect of inert gas

One of the methods to change the residence time of the reactants in the reactor is using various flow rate of inert gas. With increasing the flow rate of inert gas, the residence time of reactants in the reactor decreases. We conducted five experiments using different flow rates of nitrogen as an inert gas, diluents and carrier. Due to the lowering of the partial pressure and concentration of reactants, diluents affect the production rate of the process. With increasing the flow rate of carrier, the residence and contact time of reactants with catalyst decreases. Apparently, with increasing the flow rate of carrier in normal conditions the production rate should be decreased.

4. Conclusion

The effect of temperature and steam to DEB ratio on DVB and EVB production rate has been investigated. Temperature increases the production rate of DVB up to 620 °C. The best temperature to achieve highest production rate for DVB is 600 °C. The effect of temperature on EVB production rate is different due to complex competitive reactions occurring during the process. Increasing the steam to DEB ratio increases the production rate of DVB but decreases the production rate of EVB.

Competing Interests

Author declares that he has no competing interests.

References

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