

Research note

## Effect of Operating Conditions on Divinylbenzene Production in Diethylbenzene Dehydrogenation Reactor

M. E. Zeynali\*, H. Abedini, H. R. Sadri

Iran Polymer and Petrochemical Institute, P. O. Box: 14965-115, Tehran, Iran

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### ABSTRACT

Diethylbenzene (DEB) dehydrogenation reaction was conducted to produce divinylbenzene (DVB) and ethylvinylbenzene (EVB). The effects of temperature, catalyst weight, and time factor on the performance of the dehydrogenation reactor were investigated experimentally. Temperature varied from 550 °C to 600 °C. Temperature affects the conversion of DEB to DVB significantly. By increasing the temperature from 550 °C to 580 °C, the mole fraction of DEB at the outlet of the reactor is decreasing; however, a further increase in temperature up to 600 °C does not decrease the mole fraction of DEB at the outlet of the reactor. Catalyst weight varied from 10 g to 40 g. The results showed that the trends of EVB+DVB production and DEB consumption were identical at various catalyst weights. To obtain an optimum time factor for the DEB dehydrogenation process, experiments were conducted at various time factors. The results showed that the optimum time factor for DVB as the desired product was 825 g/h.mol. The data and information provided in this research can be used for scale-up and optimization purposes.

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### 1. Introduction

DVB is an important chemical which is used as a cross-linking agent in the polymer industry. A growing variety of applications of this material in the industry makes its production desirable for different companies.

DVB is produced by catalytic dehydrogenation of DEB at high temperatures and below atmospheric pressure in the fixed bed reactor. The catalyst is based on iron oxide and chromium oxides and some other metallic oxides. EVB is produced during the

production of DVB. The dehydrogenation reaction leading to DVB, in fact, takes place in two steps. First, DEB is dehydrogenated to EVB and, then, EVB is dehydrogenated to DVB. There exists a vinyl group in EVB which makes hydrogen detachment easier and increases its reactivity toward dehydrogenation reactions. DVB is produced more than EVB in dehydrogenation reactions due to symmetry in DEB molecules, making it more stable as a source for EVB production. In other words, EVB, which is the

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\*Corresponding author: m.zeynali@ippi.ac.ir

intermediate source for DVB production, is less stable than DEB regarding dehydrogenation reaction. Some other liquid and gaseous materials are produced during the process. Various parameters affect the preparation of DVB. The most important parameters include temperature, weight of catalyst, steam flow rate, catalyst type, catalyst pellet dimensions, pore size and pore size distribution of catalyst, and inert gas flow rate. The reaction is equilibrium limited and endothermic. Dehydrogenation reactions take place in the presence of steam. The moles of products are more than those of the reactants; with a decrease in the partial pressure of DEB, the reaction proceeds to DVB production. Therefore, at high temperatures and low partial pressure of DEB, high equilibrium conversion can be achieved. The dehydrogenation reaction of DEB follows Langmuir-Hinshelwood theory.

Theoretical research on the performance of fixed bed reactors has been reported extensively. Various methods for mathematical modeling [1-4], dynamic behavior [5-6], kinetic modeling [7], thermal behavior [8-10], control [11-13], pressure drop [14], and axial distribution [15] in fixed bed reactors have been reported in the literature. Adiabatic fixed bed reactors have been investigated in the literature [16-18]. The optimal experimental design of a catalytic fixed bed reactor [19] and a comparison of different laboratory fixed bed reactors [20] have also been reported in the literature.

There are some papers [21-25] and patents [26] in the literature about the dehydrogenation of DEB; however, scarcely applied information about dehydrogenation of this substance exists. One of the major applications of DVB is the preparation of ion

exchange beads for water purification and other uses [27-28]. Salek et al. produced monodisperse poly (styrene-co-divinylbenzene) microspheres by controlled dispersion polymerization [29]. They investigated the effects of the medium polarity based on the changing of the solvent mixture ratio and several modes of DVB addition, including simple one-shot and continuous DVB post-additions, on the particle size and morphology.

In this research, an experimental setup was designed and constructed to run DEB dehydrogenation reaction. Effects of various parameters on the reactor performance were investigated. Temperature, catalyst weight, and time factor are three essential parameters in reactor design for heterogeneous catalytic systems. The effects of these parameters on the DEB consumption and DVB and EVB production, which are practically important, have been investigated experimentally and discussed.

## 2. Experimental

### 2.1. Materials and methods

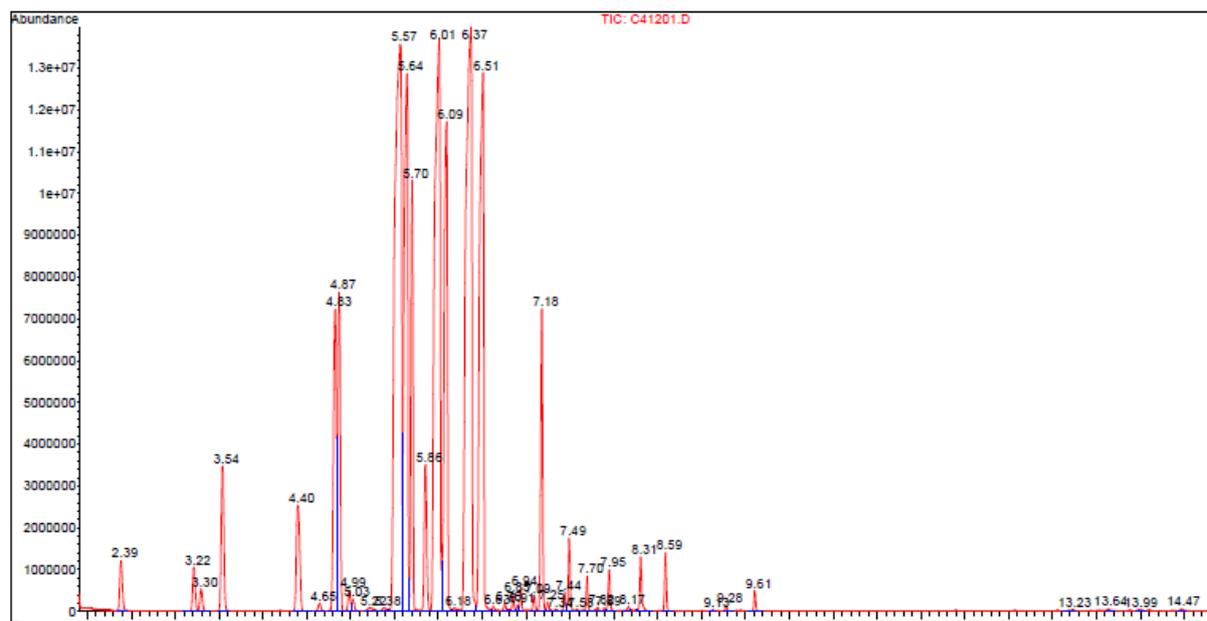
The equipment and devices used in the experiments include 1-quartz tubular reactor, 2-furnace, 3-flowmeters, 4-syringe pumps, 5-preheaters, 6-thermocouples, and 7-condenser. The heating zone of the furnace was 30 cm. Nitrogen gas was used as the carrier of the DEB and steam. The flow rate of nitrogen was adjusted to 20 cc/min for all experiments. An experimental grade of DEB was used in the experiments and purchased from Sigma-Aldrich. Liquid water and DEB were fed by two syringe pumps into the evaporator at adjusted flow rates. The ratio of water to DEB flow rate was adjusted to 5/1 for all experiments. DEB and water should be preheated before being fed to the reactor. This

was performed by two preheaters. Before conducting the experiments, the calibration of syringe pumps and accuracy of flow rates were ensured. The fixed bed tubular reactor was loaded with catalyst pellets. The loaded reactor was kept for 24 h at 600 °C to activate the catalyst to run the experiments. Quartz beads were used in front of the catalyst pellets bed to ensure uniform heat transfer and flow to prevent channeling of the gaseous reactant and hot spot formation in the reactor. At the end of the reactor, a quartz condenser was used to condense the products. The liquid products were collected by a balloon at the bottom of the condenser. The collected liquid had two phases: hydrocarbon and aqueous phases. Two phases were separated by a

decanter and hydrocarbon phase was sent for analysis by GC-mass. Then, 10, 20, 30, and 40 g catalysts were used in the experiments. Temperatures of 550, 560, 570, 580, 590, and 600 °C were used in the experiments. Keeping the water to DEB flow rate ratio constant, the flow rate of DEB varied from 5 cc/h with 1 cc/h increment to 10 cc/h. KS-4 (commercial name of the catalyst) dehydrogenation catalyst was used in this study. The catalyst was provided by Pars Petrochemical Complex. The photo of the experimental setup is presented in Figure 1. A typical GC-mass spectrum and chemical analysis of the products are shown in Figure 2 and Table 1, respectively.



**Figure 1.** The photo of the experimental setup.



**Figure 2.** GC-mass spectrum for the sample prepared at 600 °C and 40 g catalyst.

**Table 1**

GC-mass analysis results for liquid products at 600 °C and 40 g catalyst.

Substance	Weight %
DEB	15.22
EVB	26.4
DVB	47.88
Styrene	0.6
1-Ethyl 3- Methyl Benzene	0.91
1-Ethenyl 3-Ethyl Benzene	3.1
1-ethenyl 4-Methyl Benzene	2.95
2-Methyl 1-Propen Benzene	0.36
Naphthalene	2.58

### 3. Results and discussion

#### 3.1. The effect of temperature

As is known, temperature affects the dehydrogenation reaction significantly. To investigate the effect of temperature, various runs at 550 °C to 600 °C are conducted. Figures 3 to 5 include 40 g catalyst and 5/1 the ratio of water to DEB. Considering the constant catalyst weight and flow rate of DEB and water, the time factor was kept constant and remained at 621.34 g h/mol. As is seen in Figure 3, the mole fraction of DEB is reducing up to 580 °C, which is due to the

dehydrogenation reactions. A further increase in temperature up to 600 °C does not decrease the mole fraction of DEB. Due to the thermal cracking reactions above 600 °C, we did not conduct the experiments above 600 °C. As is seen in Figure 4 for EVB production, initially, there is a gradual surge up to 590 °C. There are two competitive reactions: the detachment of hydrogen from DEB giving EVB and detachment of hydrogen from EVB giving DVB. One reaction produces EVB, and the other consumes EVB and produces DVB.

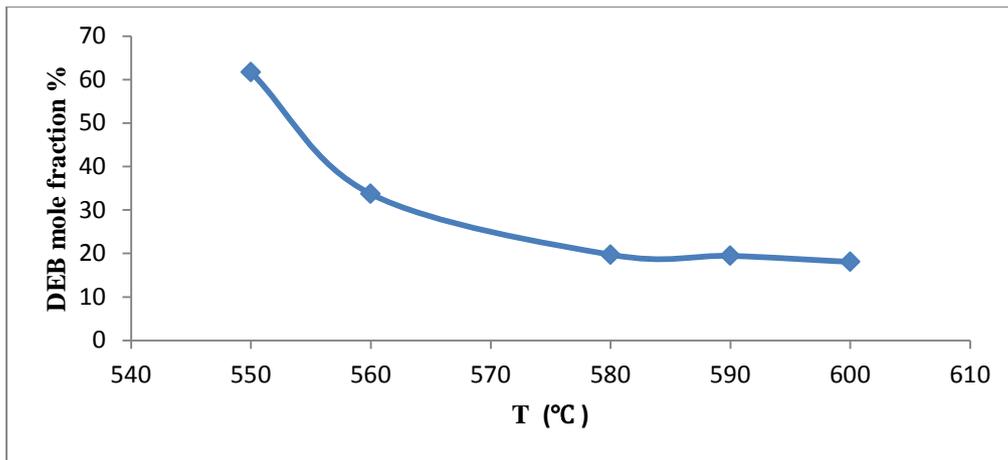


Figure 3. DEB mole fraction in the outlet of the reactor vs. temperature.

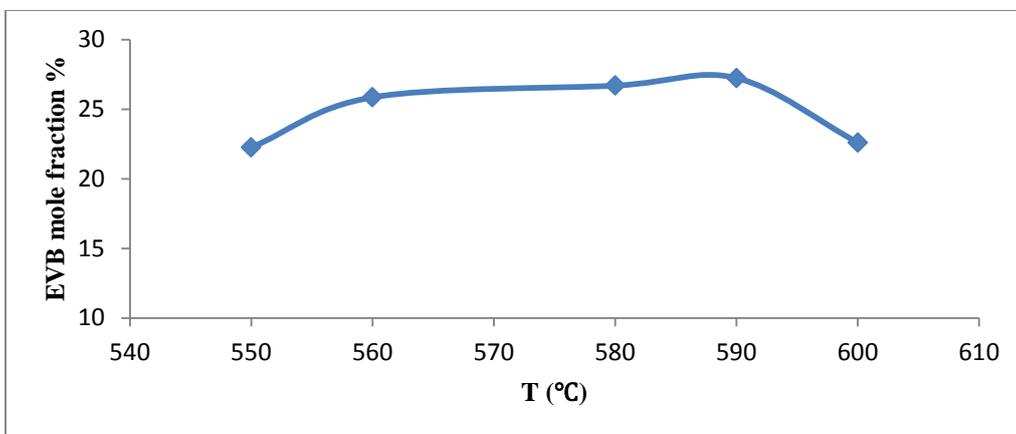


Figure 4. EVB mole fraction in the outlet of the reactor vs. temperature.

The overall result of these two reactions increases the mole fraction of EVB up to 590 °C. Above 590 °C, the consumption of EVB is higher than its generation; therefore, the mole fraction of EVB reduces and leads to more DVB formation. The corresponding reasons

are shown in Figure 3. Because the generated amount of EVB proportional to DEB consumption reaches a constant amount (see Figure 3) and, as is seen in Figure 5, the amount of DVB increases, the reduction of EVB at this temperature interval is obtained.

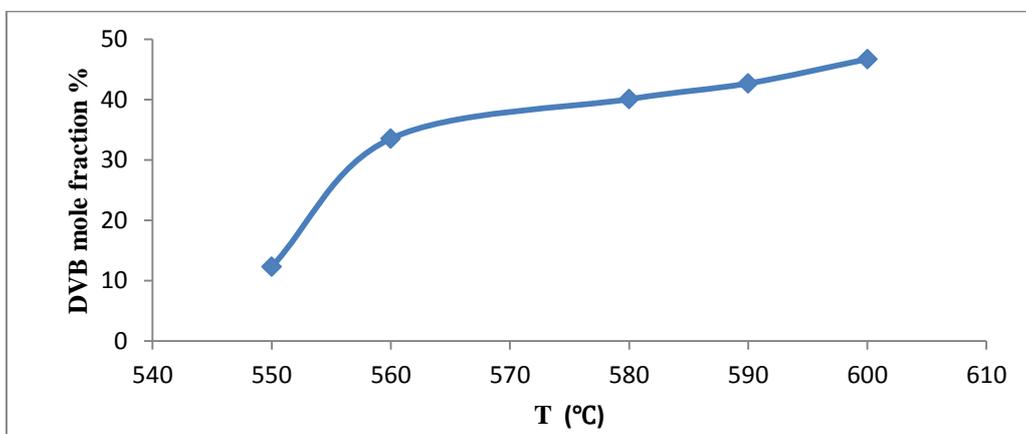
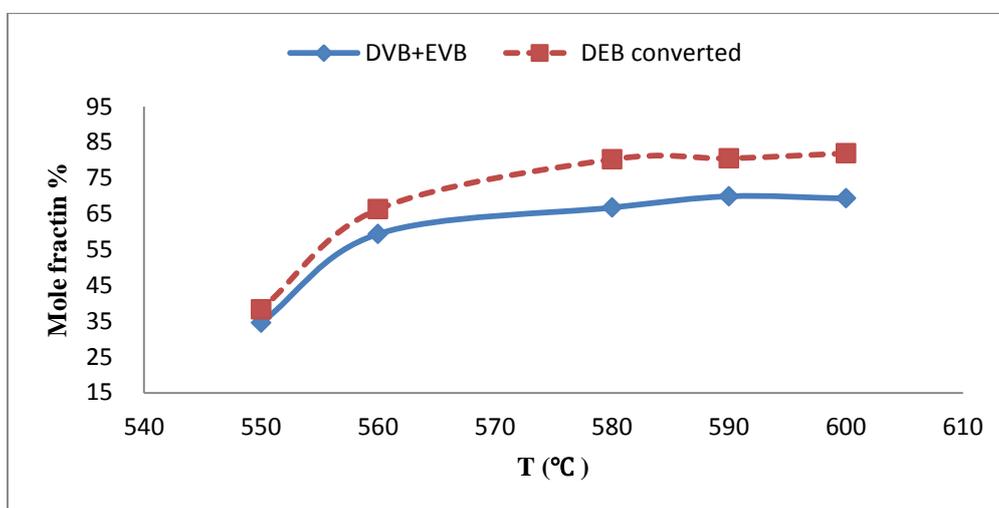


Figure 5. DVB mole fraction in the outlet of the reactor vs. temperature.

According to Figure 5, the DVB production and temperature are directly related; in other words, an increase in temperature facilitates the detachment of hydrogen from EVB. The slope of the curve in Figure 5 is high before 580 °C, and the mole fraction of DVB reaches a maximum value at 600 °C.

In Figure 6, conversion of DEB and total mole fractions of EVB and DVB at the outlet of the reactor are presented. As is seen, the trend of changes of mole fractions is the same, presenting consumed DEB that has been converted to EVB and DVB. There is a

difference between these two curves due to the generation of light hydrocarbon as by-products (products other than EVB and DVB). These by-products are shown in Table 1. The gap between the two curves is small at 550-560 °C. Therefore, the production of light hydrocarbons as by-products is less in this range of temperatures. The production of by-products at 580-600 °C is high, showing that with an increase in the temperature, the side reactions increase, too. If side reactions do not take place, the two curves in Figure 6 should overlap.



**Figure 6.** Converted DEB and produced EVB+DVB mole fraction in the outlet of the reactor.

### 3.2. The effect of catalyst weight

Investigation of the effects of catalyst weight on reactor performance is always important. In this section, the effect of catalyst weight on the conversion was investigated at 600 °C and 5/1 ratio of the water to DEB flow rate. In these experiments, 10, 20, 30, and 40 g catalysts were used in the reactor. As is seen in Fig. 7, DEB consumption increases with an increase in catalyst weight. Apparently, at a constant flow rate with an increase in catalyst weight, the active site surface increases, which leads to high consumption of DEB. Catalyst weight has an optimum amount, and an increase in catalyst weight above the

optimum amount is not justifiable from an economic point of view. Due to the limitation of reactor volume, the effect of catalyst weight has not been investigated at a higher catalyst weight. This effect can be investigated by changing the flow rate of reactants, as investigated in the next section. For a better presentation of the effect of catalyst weight on the mole fraction of products, the mole fractions of DVB and EVB are presented simultaneously in Fig. 8. As is seen, the mole fraction of DVB is more sensitive to catalyst weight than EVB, and its slope is higher.

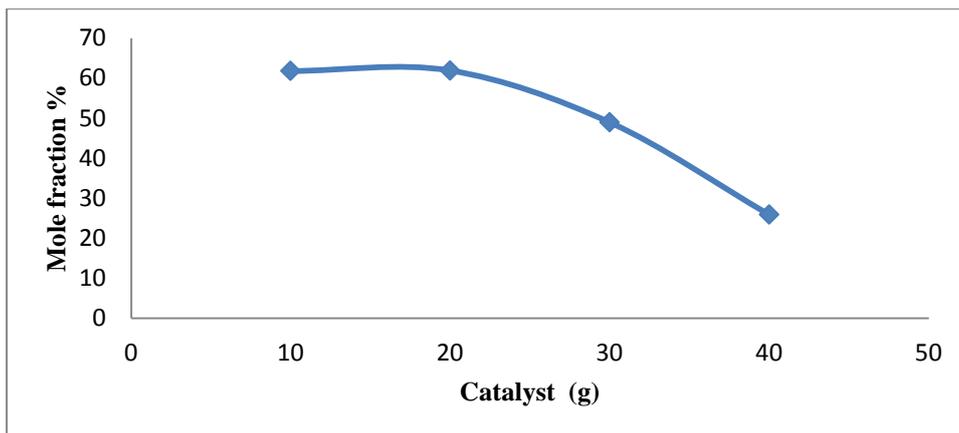


Figure 7. Effect of catalyst weight on the mole fraction of DEB at the outlet of the reactor.

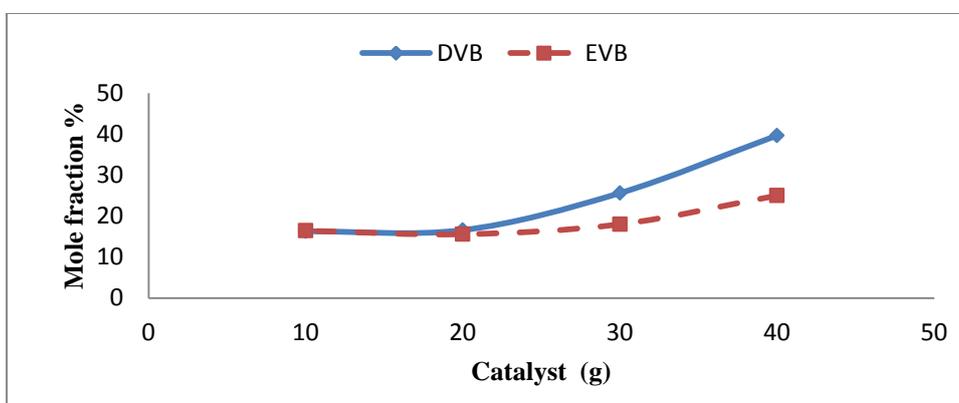


Figure 8. Effect of catalyst weight on the mole fraction of DVB and EVB at the outlet of the reactor.

Fig. 9 shows that the trends of EVB+DVB production and DEB consumption are identical. This means that with an increase in catalyst weight, the reaction proceeds toward DVB and EVB production. This can be seen in the distance which exists between the two curves, as shown in Fig. 9. The distance shows the production of light hydrocarbons other than DVB and EVB as by-products. As is seen, the distance between DEB conversion and EVB+DVB production remains constant with an increase in the catalyst weight from 10 gr to 40 g. Therefore, it can be concluded that the amount of by-products is independent of catalyst weight, yet depends on temperature. The optimum weight of catalyst is required to determine the optimum dimensions of the reactor for the industrial-scale production. In the industrial-scale

operations, two or three adiabatic reactors are used. It is possible that the reason for using several reactors with less catalyst instead of one reactor with more catalyst lies in the pressure drop problems in one large reactor. Another problem with a single reactor is the higher decrease of temperature along the reactor due to the endothermic reaction. The reduction of temperature in the large single reactor can reduce the conversion significantly. The reactors can be of axial or radial flow. In radial flow reactors, the pressure drop is low. On the experimental scale, normally, isothermal reactors are used. In fact, increasing the weight of catalyst increases the effective volume of the reactor. The main goal of investigating the effect of the amount of the catalyst at a constant flow rate of DEB is to determine the maximum

limit of catalyst amount, beyond which the conversion does not increase. The practical range of this maximum conversion is below the equilibrium conversion at a certain temperature. How much closer we get to the equilibrium conversion presents the quality of the process conditions that have been defined

and used. Increasing the amount of the catalyst and flow rate of DEB has a similar effect on hourly space velocity. In the industrial-scale operations, the capacity of the plant is fixed; therefore, to increase the conversion, the amount of the catalyst should be adjusted.

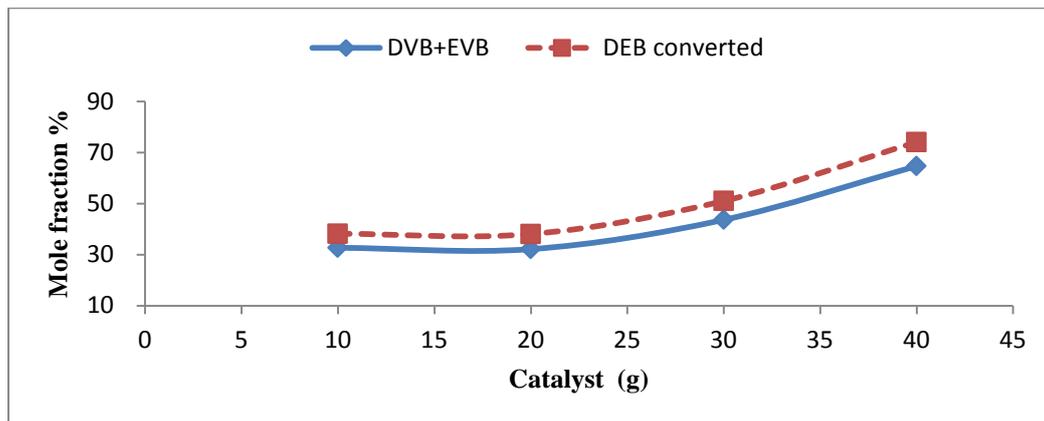


Figure 9. Converted DEB and produced DVB+EVB at the outlet of the reactor versus catalyst weight.

### 3.3. The effect of time factor

With variations of catalyst weight or flow rate of DEB, the performance of reactor can be investigated with respect to various time factors. Figure 10 shows that the mole fraction of DEB at the outlet of the reactor does not change very much in low time factors. This trend is observed in Figure 7 when the effect of catalyst weight on DEB conversion is investigated. Above 840 g/h.mol, the mole fraction of DEB at the outlet of the reactor remains constant and

does not depend on the time factor. This time factor can be used to design the optimum performance of DEB dehydrogenation reactor. Variations of EVB mole fraction at the outlet of the reactor in terms of time factor are shown in Figure 11. Since EVB is an intermediate to produce DVB, the curve of mole fraction vs. time factor passes through a maximum. The optimum time factor for EVB production is 650 g/h.mol. In this time factor, the mole fraction of EVB is maximum at the outlet of the reactor.

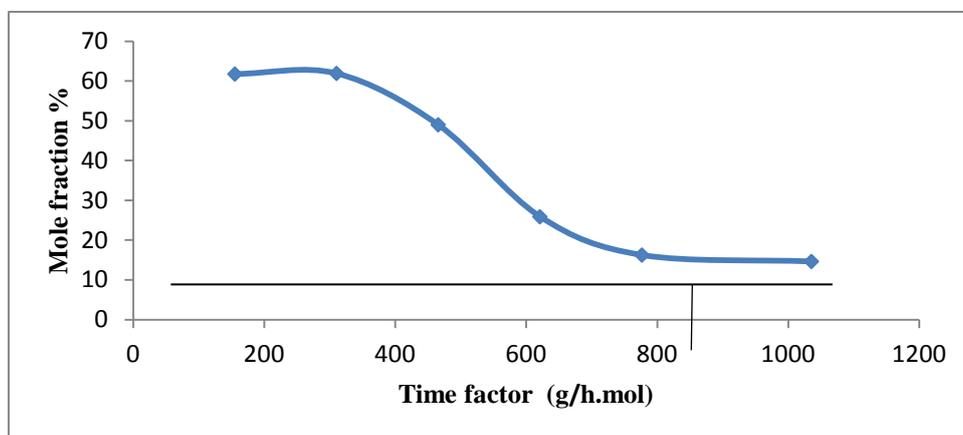
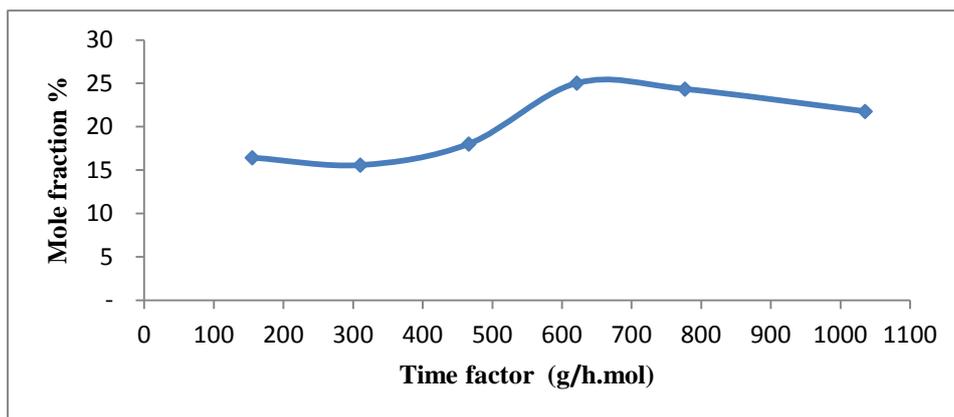


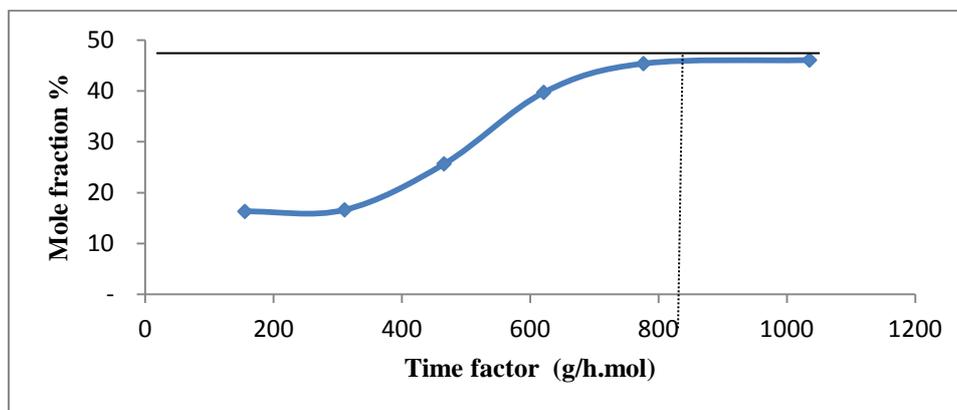
Figure 10. DEB mole fraction versus time factor at the outlet of the reactor.



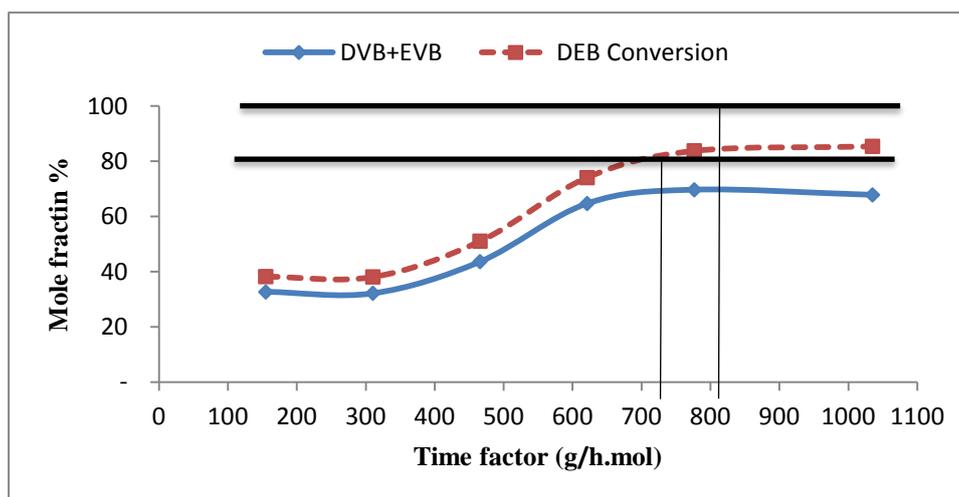
**Figure 11.** Mole fraction of EVB at the outlet of the reactor versus time factor.

Figure 12 demonstrates the trend of DVB production in terms of time factor. The curve in Figure 12 has three different sections as DEB consumption curve in terms of time factor. The optimum time factor for DVB production is 825 g/h.mol. Above this time factor, the mole fraction of DVB does not change with an increase in time factor. Since the main purpose of DEB dehydrogenation is DVB production, this time factor can be considered as the optimum time factor for the process. With the known DEB flow rate, the weight of the optimum catalyst can be determined; conversely, the optimum flow rate of DEB can be calculated when the catalyst weight is known. In Figure 13, the consumption of DEB and the production of EVB+DVB are plotted in terms of time factor. The trends of curves are identical, and both of them approach a plateau section when

the time factor increases. The curves do not overlap, and the gap between them again shows the generation of light hydrocarbons as by-products during the dehydrogenation process. In the open literature, there is little information about the production of DVB with quantitative data. This presents the novelty of this research. Only Foni et al. investigated the kinetics of DEB dehydrogenation [24]. They used a catalyst which is different from that used in this research. They presented some data on the conversion of DEB using a differential reactor. They did not use mixed DEB including all isomers for dehydrogenation. They used para-DEB. A typical result of experiments of Forni et al. is shown in Table 2. Their results cannot be compared with those obtained in this research, because the catalyst and feed composition are different.



**Figure 12.** Mole fraction of DVB at the outlet of the reactor versus time factor.



**Figure 13.** Converted DEB and produced DVB+EVB at the outlet of the reactor versus time factor.

**Table 2**

A typical Foni et al., run data [24].

Temperature (°C)	490
p-DEB feeding rate (mmol/h)	9.03
p-EVB feeding rate (mmol/h)	1.33
Water feeding rate (mmol/h)	336.11
Catalyst weight (mg)	87.0
Product analysis (mol %)	
Light hydrocarbon	0.255
p-DEB	86.817
p-EVB	12.724
p-DVB	0.204

#### 4. Conclusions

In this research, the main goal was to investigate the effect of three key parameters on the performance of the DEB dehydrogenation reactor experimentally. The effect of temperature, catalyst weight, and time factor on the consumption of DEB and productivities of DVB and EVB in the reactor was investigated and discussed. With an increase in temperature, DEB consumption and DVB productivity increased. By increasing the catalyst weight under a similar condition, the productivity of DVB and EVB increased. This increase in DVB is more than that in EVB. The results of the effect of time factor, temperature, and catalyst weight on reactor performance showed that the best

operating condition comprises 600 °C, 40 g of catalyst weight, 9 cc/h of DEB flow rate, and 45 cc/h of water flow rate.

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