Dehydrogenation of Ethylbenzene sing CO_2 – A Process Design Study

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The scope in this project is the design of a dehydrogenation process for ethylbenzene using CO_2 as mild oxidant including a technical and economical evaluation. Compared to the conventional process this process has a more favorable equilibrium and can therefore be operated at a lower temperature and lower energy consumption. The design is based on the data of the most promising catalyst investigated which is Fe/Al/Zn (1/2/6) reported by Mimura (2002). Laboratory results show a single pass conversion of 26% with a selectivity to styrene of 91% for a CO_2/ethylbenzene ratio of 11. The process is designed according to the systematic process synthesis techniques. Results show that the low conversion and especially the high CO_2/ethylbenzene ratio results in an unfeasible recycle flow. It is decided to reduce the CO_2/ethylbenzene ratio to 2. The economic evaluation shows that the current margin of $200 between the product and raw material is too low and should be minimal $250. An alternative would be to increase the selectivity to minimal 93%. The available catalyst data such as selectivity, conversion and lifetime is limited and should be subject of further research especially at low CO_2/ethylbenzene ratios.

1. Introduction

The objective of this project is to show the systematic design of a new process for the production of styrene from ethylbenzene based on the oxidative dehydrogenation of ethylbenzene with carbon dioxide. The dehydrogenation reaction of ethylbenzene is an endothermic reaction and for the conventional process characterized by a high selectivity towards styrene and a conversion of 60-70 % per pass. Superheated steam is used as a heat source. Recently, research has focused on the dehydrogenation of ethylbenzene with mild oxidants such as nitrous oxide and carbon dioxide. Towler and Lynn (1994) demonstrated the possibilities of an equilibrium shift for ethylbenzene dehydrogenation through coupling with the reverse water-gas shift reaction. For this equilibrium shift carbon dioxide is used. One of the advantages of the reaction with carbon dioxide is that it can take place at a lower temperature, due to the equilibrium shift.

2. Chemistry and process overall

Reactions

The reaction from ethylbenzene to styrene using CO_2 can occur along two pathways. The one-step pathway reaction is given in reaction 1.

$$C_8H_{10} + CO_2 \Leftrightarrow C_8H_8 + CO + H_2O \qquad \Delta H_R = 125 \text{ kJ/mol} \qquad \text{Reaction 1}$$

In the two-step pathway the reaction to styrene is coupled with the reverse water-gas shift reaction as given in reaction 2 and 3.

$$C_8H_{10} \Leftrightarrow C_8H_8 + H_2 \qquad \Delta H_R = 125 \text{ kJ/mol} \qquad \text{Reaction 2}$$

$$H_2 + CO_2 \Leftrightarrow CO + H_2O \qquad \Delta H_R = 35 \text{ kJ/mol} \qquad \text{Reaction 3}$$

Which pathway dominates, depends on the type of catalyst. In the reactor two side reactions take place. First, the reaction from ethylbenzene to benzene and ethylene and second the reaction of ethylbenzene and hydrogen to toluene and methane.

$$C_8H_{10} \Leftrightarrow C_6H_6 + C_2H_4 \qquad \text{Reaction 4}$$

$$C_8H_{10} + H_2 \Leftrightarrow C_7H_8 + CH_4 \qquad \text{Reaction 5}$$

In Table 1 a comparison is made between reactor properties of the conventional process and the carbon dioxide process. Critical will be the reported CO_2/EB ratio of 11:1 which will result in a large CO_2 recycle.

Table 1: Comparison conventional and CO_2 process (Mimura, 1998 and Chon, 2003).

Property	Conventional process	CO_2 process
Temperature of the reactor	650 – 800 $^{\circ}$C	500 – 580 $^{\circ}$C
Reactor operation	isotherm/adiabatic	to be decided
H_2O/EB ratio, resp. CO_2/EB	1:1 to 4:1	11:1
Heat per kg of styrene	6.6 MJ/kg	2.7 MJ/kg

Catalyst

Based on an extensive literature research, the Fe/Al/Zn (1/2/6) catalyst is chosen for the process (Mimura, 2002). Some properties of the catalyst are mentioned in Table 2. The performance of the catalyst was only available at a temperature of 823 K, and a pressure equal or lower than 1 atmosphere, a carbon dioxide to ethylbenzene ratio of 11:1 and 25.7% conversion.

Table 2: Catalyst properties (Mimura, 2002)

Components (molar ratio)	Surface area (m^2/g)	Conversion of Ethylbenzene (%)	Selectivity (%)		
			Styrene	Benzene	Toluene
Fe/Al/Zn (1/2/6)	22.1	25.7	91.4	6.2	2.3

Process alternatives

The functions of the reactants, the heat capacity, the advantages and disadvantages of this process are also summarized in Table 3.

Based on the comparison it is worthwhile to investigate the use of the carbon dioxide process. The opportunities lie in the area of energy consumption in the reactor, the equilibrium shift by the water-gas shift reaction, the absence of vaporization/ condensation of carbon dioxide and the possible higher yield of styrene. The catalyst deactivation, the side reactions, polymerization, heat supply and the large carbon dioxide recycle are points that could be a disadvantage of the carbon dioxide process.

Table 3: Steam, oxygen and carbon dioxide process comparison (adapted from Chon, 2003 and Mobil Oil Corporation, 1973)

Characteristics	Steam	Carbon dioxide
Function	Not oxidant, diluent	Soft oxidant, diluent
Conversion of EB	65 %	25.7 %
Selectivity to ST	±90 % and higher	91.4 %
Heat capacity	Medium, 37 J/mol.K at 673 K	High, 49 J/mol.K at 673 K
Advantage	High selectivity	High selectivity
	Catalyst stability	Activity enhancement
	Coke resistance	Equilibrium shift
	Keeping oxidation state	Cheap carrier gas
Disadvantage	Expensive diluents	Not commercialized
	Endothermic (±120 kJ/mol)	Endothermic (±160 kJ/mol)
	High latent heat	Catalyst deactivation
	High operation costs	

Process overall

The design of the process is started with process overall calculations assuming 100 % overall conversion of ethylbenzene and 97 % selectivity to styrene which gives the amount of raw material needed and the amount of byproduct produced for the given styrene plant capacity. Next the economical feasibility is checked based on product sales and raw material costs. The high selectivity is reported by several researchers for small scale units. Given the prices assumed about 80 % yield to styrene is needed for an economically feasible process. If this is technically possible has to be checked during the design.

3. Process design

The process design procedure applied is according to a systematic stepwise and iterative procedure going from process overall, to conceptual design, and to the final process flowsheet. In each step several alternatives need to be evaluated and documented. A more detailed design combined with mass balance calculations is obtained, going from functions (reaction, separation, Figure 1) to selection and design of unit operations. At the final stage a process design with detailed mass and energy streams in a commercial flowsheeter (UniSim ®) is generated. For this project several alternatives in the reaction and separation parts have been considered. One of the alternatives is shown in Figure 1 reduce this ratio comparable to the development of the steam process. Therefore the

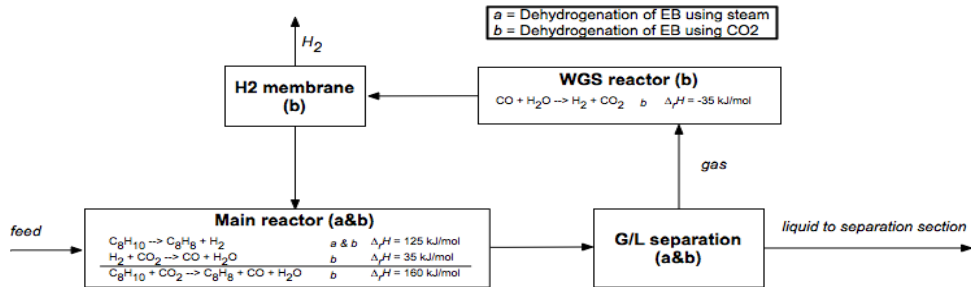ratio is adjusted to 2. Calculation results show a reactor outlet composition as shown in Table 4.

a = Dehydrogenation of EB using steam
b = Dehydrogenation of EB using CO2

H2 membrane (b) — H_2

WGS reactor (b)
$CO + H_2O \rightarrow H_2 + CO_2$ b $\Delta_r H$ = -35 kJ/mol

gas

feed →

Main reactor (a&b)
$C_8H_{10} \rightarrow C_8H_8 + H_2$	a & b	$\Delta_r H$ = 125 kJ/mol
$H_2 + CO_2 \rightarrow CO + H_2O$	b	$\Delta_r H$ = 35 kJ/mol
$C_8H_{10} + CO_2 \rightarrow C_8H_8 + CO + H_2O$	b	$\Delta_r H$ = 160 kJ/mol

G/L separation (a&b) → liquid to separation section

Figure 1: Functional block flow diagram for the ethylbenzene to styrene process

Table 4: composition of reactor outlet stream for a feed containing 10900 kmol/h CO_2 and 5460 kmol/h EB.

molflow	H_2	CH_4	$C_2^=$	CO	CO_2	H_2O	Tol.	Benz.	EB	ST
kmol/h	0	24	87	1260	9590	1260	24	96	4060	1280

Reactor design

For a reliable design of the reaction function for a specific catalyst consistent data for conversion, selectivity and kinetic data are needed. A complete data set for a high-conversion catalyst is not available in open literature. The Fe/Al/Zn-catalyst of Mimura (2002) tested at laboratory conditions is chosen to design the reactor. However, due to the catalyst's conversion per pass of 25.7 % the recycle is too large for economical realization. Therefore the design is repeated for an EB conversion per pass of 90% and selectivities according to Table 2 assuming that for the catalyst more optimal conditions exist. The reactor design criteria lead to the selection of a fluidized bed operated at 550 °C. Unfortunately it cannot run adiabatically by heating only the feed, thus implying the need for external heating. Reactor design resulted in a fluid bed of 18 m diameter and 36 m height. This is too large for one single unit and has to be split in several parallel units.

Heat integration:

Energy conservation is important for the process design. Cooling and heating costs are a significant part of the total costs of the preliminary design. Heat integration can be an important way to lower these costs. For this process 11 streams must be cooled (7) or heated (4). These streams will be used in the heat integration. Three possibilities are considered: without heat integration, with minimum energy addition and with the lowest installation cost, which equals the lowest area (see Table 5).

Economics

In this part the economics of the process is evaluated to know whether this process is feasible or not. Included in this evaluation are:

- Production cost
  - Direct cost: Raw materials (the price of ethylbenzene is estimated at $1270/t), catalyst, utilities, labour and maintenance

- Indirect cost: fixed cost (depreciation is based on a period of 10 years), plant overhead, general cost
- Capital cost (estimation based on a factor method is 500 M$)
- Sales (the price of styrene is estimated at $1445/t).

Based on the economic evaluation it is concluded that the process is not profitable. To improve the process economics up to the point of break even the margin between styrene and ethylbenzene should increase to minimal $250/t at 90% selectivity or given a margin of $200/t the selectivity to styrene should increase to at least 93%.

Table 5: Summarized values of the heat integration

	Without Heat Integration	Minimum duty	Lowest area
Number of Heat Exchangers	11	18	12
Duty (MW)	1114	395	473
Duty for cooling (MW)	419	60	99
Duty for heating (MW)	695	335	374
Area needed (x10^3 m^2)	202	180	128

4. Discussion

In the developed base case scenario, carbon dioxide is acting as heat transfer agent and oxidizing intermediate which is fully recovered and re-used in the reaction. Hydrogen is recovered from the dehydrogenation process using a water-gas shift reactor and a membrane. The found advantages and disadvantages of the complete process design are summarized in Table 6.

Table 6: Summary of advantages and disadvantage of dehydrogenation of ethylbenzene using carbon dioxide versus the conventional process (using steam)

Aspect	Carbon dioxide	Steam (conventional process)
Reaction enthalpy	More endothermic	Less endothermic
Hydrogen production	Yes	No (but can be implemented)
Catalyst	More data needed	Good catalysts available
Equilibrium	Is shifted towards styrene due to reverse WGS	Cannot be shifted
Waste products	No waste water	Waste water
Separation of reactor effluent	Difficult to separate lights due to gaseous CO_2	Less difficult; water can be phase separated
Gas recycle	Yes	No
Polymerization control	Indirect cooling in reactor outlet condenser. Hence not so good control.	Direct & sudden cooling by quenching reactor outlet with water already available in system. Hence better control.

From an energy-wise point of view, carbon dioxide has the advantage over steam that it will not be condensed/evaporated during the total process. But reactions are more endothermic than in the conventional process due to the use of the endothermic reverse

water-gas shift reaction. Operating temperature of the reactor is on the other hand lower than in the conventional process. Using a water-gas shift reactor, some of the energy lost due to the reverse water-gas shift reaction in the main reactor could be recovered.

The reactor design reveals that an industrially viable reactor cannot be operated adiabatically by only heating the feed stream. Calculations also show that the single pass conversion of 26 % is too low and results in a too large gas recycle flow which makes the process unfeasible. The single pass conversion should be increased, preferably to 90 %. Since carbon dioxide is a gas which is difficult to separate from the gas recycle stream, the whole stream (except hydrogen) is recycled to the reactor. The conventional process, which uses steam that condenses to liquid water, does not exhibit such a gas recycle stream since the liquid water can easily be recycled. The base case simulation is operated at a carbon dioxide/ethylbenzene ratio of 2, which is already very low. However, reliable information about a better catalyst could increase reactor yield and thus decrease recycle streams.

5. Conclusions

The developed carbon dioxide process is technical feasible but can only be profitable when better catalysts are developed with a selectivity of minimal 93% for a given margin of 200$/t of product. Furthermore, the conversion per pass should be increased to preferable 90 % to reduce the recycle flow. Also the ratio of CO_2 to ethylbenzene needs to be reduced from the reported factor 11 to maximal 2 to avoid excessive recycle flows of CO_2.

Acknowledgement

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