

## INTEGRATED PROCESS FOR $\gamma$ -BUTYROLACTONE PRODUCTION

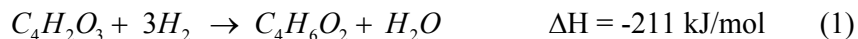
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*An integrated process for the production of  $\gamma$ -butyrolactone by coupling maleic anhydride hydrogenation and 1, 4-butanediol dehydrogenation in a fixed bed adiabatic reactor is studied. The reaction conditions realizing optimal hydrogen utilization and better energy efficiency are determined. Compared to stand-alone processes, the integrated process has several advantages, such as simpler reactor, easy temperature control, improved  $\gamma$ -butyrolactone yield, good energy efficiency and optimal hydrogen utilization. The integrated plant shows robust behavior with respect to disturbances and allows production rate change.*

**Keywords:**  $\gamma$ -butyrolactone, reaction coupling, process design and control.

### 1. Introduction

$\gamma$ -butyrolactone (GBL) is known as a versatile solvent and a raw material for the synthesis of pyrrolidone, N-methyl pyrrolidone, N-vinyl pyrrolidone, herbicides, and rubber additives. GBL is manufactured via two methods: hydrogenation of maleic anhydride (MA) and dehydrogenative cyclization of 1,4-butanediol (BDO). Both processes are typically performed in multi-tubular fixed-bed reactors [1]. The catalytic hydrogenation of MA or its derivatives such as maleic acid, succinic anhydride or succinic maleate to GBL has frequently been reported in the literature [2]. The reaction equation of MA hydrogenation to GBL can be represented as follows:



It is obvious from equation (1) that production of 1 mole of GBL requires 1 mole of MA and 3 moles of  $H_2$ , releasing 211 kJ of heat. Owing to the strong exothermic nature of the reaction, it is difficult to control the temperature of the process. In a tubular fixed-bed reactor, this might cause thermal runaway, lead to apparent hotspots and low selectivity to the desired product, GBL. A large excess of hydrogen is needed.

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The vapor phase catalytic dehydrogenation of BDO to GBL has also been described in the literature [3]. This reaction can be expressed as follows:



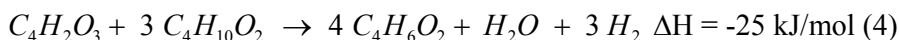
From equation (2) it is evident that production of 1 mole of GBL requires 1 mole of BDO, releasing 2 moles of  $H_2$  and requiring 61.6 kJ of heat. The hydrogen released from reaction cannot be used properly in a single dehydrogenation process.

The new catalytic process proposed in this work combines reactions (1) and (2) into one coupled system which can significantly improve the yield of the catalytic hydrogenation of MA, apart from the better thermal balance and the effective usage of hydrogen through hydrogen transfer between the two reactants. In addition, this new integrated process produces one desired product (GBL) with a substantially increased hydrogenation yield. The new combined reaction can be expressed as follows:



The MA to BDO ratio used in the process is 1:1.5 to balance the hydrogen consumed and produced in the system. Due to this perfect hydrogen balance it was expected to easier control of the reactor temperature due to less heat released as compared to individual MA hydrogenation. From equation (3), it can be noted that 2.5 mole of GBL requires 1 mole of MA and 1.5 moles of BDO.

The system can also be coupled on the basis of balancing heat. The combined reaction can be expressed as follows:



From equation (4) it can be noticed that 4 moles of GBL requires 1 mol of MA and 3 moles of BDO. The MA to BDO ratio used in the process is 1:3 to balance the heat consumed and produced in the system. Due to this almost perfect heat balance the adiabatic operation of the chemical reactor becomes an attractive option.

The combined system for hydrogenation of MA and the dehydrogenation of BDO could be carried out over the same Cu-based catalyst, and under similar reaction conditions. The reaction kinetics used for the simulations are extracted from the literature based on Cu-Zn-Al catalyst:

Maleic anhydride hydrogenation [4]:

$$k_1 = 4.68 \times 10^5 \cdot \exp(-5800/T) \quad \text{kmol} \times \text{m}^{-3} \times \text{s}^{-1} \times \text{Pa}^{-1} \quad (5)$$

1, 4-butanediol dehydrogenation [5]:

$$k_1 = 2.57 \times 10^{17} \cdot \exp(-262/T) \quad \text{kmol} \times \text{m}^{-3} \times \text{s}^{-1} \times \text{Pa}^{-1} \quad (6)$$

The coupled reactions can be performed at temperatures which are 30–50 °C less as compared to individual reaction, because the active hydrogen species on the catalyst surface from BDO dehydrogenation promotes the MA hydrogenation reaction [6], [7]. The coupling may lead to advantages, such as good energy efficiency, the easy temperature control in an adiabatic reactor due to its moderate heat release compared with the single reaction processes which can avoid the formation of apparent hotspots or cold spots [6], [7].

The previous studies [6], [7] considered the possibility of coupling these reactions taking into account only the reactor. However, no plantwide design and control results have been reported. The goal of this paper is to fill this gap by presenting details of an integrated process for 1,4-butanediol (BDO) dehydrogenation and maleic anhydride (MA) hydrogenation, to produce one valuable product,  $\gamma$ -butyrolactone (GBL). The advantages of optimum hydrogen and energy utilization, reduced parametric sensitivity, dynamic stability and safe operation are emphasized. Our conclusions are supported by rigorous steady state and dynamic simulations performed in Aspen Plus and Aspen Dynamics. Conclusion and final remarks end the paper.

## 2. Integration by Hydrogen Balance

This section presents a process which couples dehydrogenation of 1,4-butanediol and hydrogenation of maleic anhydride in a single adiabatic reactor. The benefit of coupling the exothermic and endothermic reactions (hydrogenation and dehydrogenation) is that the heat generated by the first reaction is taken up by the second one, and no additional heating or cooling arrangements are required in the system. This leads to a much simpler reactor and the parametric sensitivity of the reactor is greatly reduced. The conversion of both maleic anhydride and 1, 4-butanediol is > 99.5%, eliminating recycling of reactants. Fig. 1 presents the flowsheet of the integrated maleic anhydride hydrogenation and 1, 4-butanediol dehydrogenation process. Reactants (MA – 20 kmol/h, BDO – 30 kmol/h and hydrogen – 5000 kmol/h) are mixed and brought to reaction temperature (210 °C). The reactions take place in a tubular reactor (5 m diameter, 3 m length) which is adiabatically operated. The reactor is designed for total conversion of reactants. Stream table of the process is given as Table 1. Fig. 2 shows mole fraction and temperature profiles along the reactor. The conversion of reactants into products is uniformly distributed along the reactor length and almost constant temperature should be remarked.

The reactor outlet is cooled to 20 °C and vapor – liquid separation is performed. As the complete conversion ( $> 99.5\%$ ) of reactants is achieved, there is no recycling of reactants simplifying technical difficulties. A high boiling point difference between water and GBL results in easier separation by distillation. GBL is obtained as a product at the rate of 49.6 kmol/h with high purity  $> 99.5\%$ . In theory, the plant is best operated at MA: BDO = 1: 1.5 with very high ratio of hydrogen: feed = 100:1 to 200:1. Perfect balancing of hydrogen consumption / generation in the two reactions is impossible in practice. Therefore, a small amount of fresh and purge hydrogen streams are provided for better control purposes.

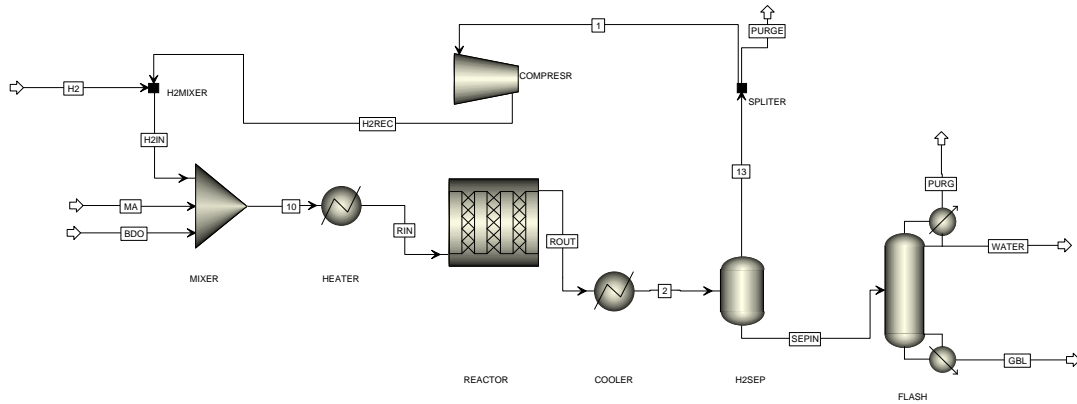


Fig. 1. Integrated Process

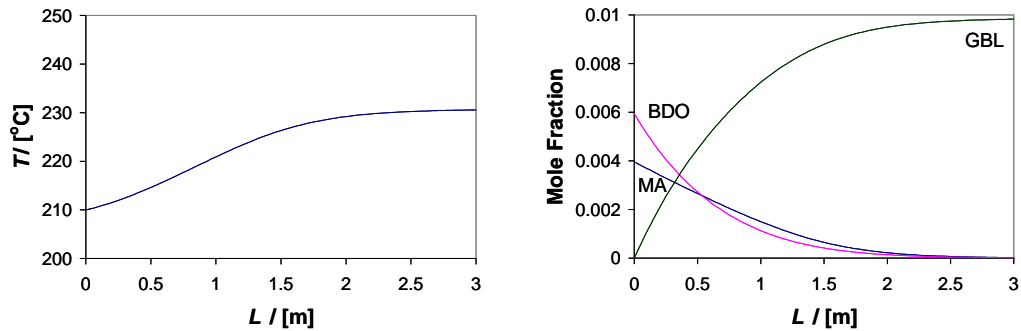


Fig. 2 Temperature and Molar Profile

Table 1

Stream Table (Hydrogen Balance)								
	MA	BDO	GBL	H2REC	RIN	ROUT	SEPIN	WATER
Temperature ( $^{\circ}\text{C}$ )	25	25	20	20	210	230.3	20	20
Pressure (bar)	1.5	1.5	1.2	1.2	1.5	1.5	1.2	1.2
Vapor Fraction	0	0	0	1	1	1	0	0.001
Mole Flow (kmol/hr)	20	30	49.62	4548	5098	5118	64.56	14.94
Mole Fraction								
Hydrogen	0	0	0	0.989	0.981	0.977	0	0.001
Water	0	0	0	0.01	0.009	0.013	0.228	0.984
MA	1	0	0	0	0.004	0	0.002	0.007
GBL	0	0	1	0	0	0.01	0.769	0.003
BDO	0	1	0	0	0.006	0	0.001	0.005

### 3. Integration by Heat balance

Reactants (MA – 20 kmol/h, BDO – 60 kmol/h and hydrogen – 3200 kmol/h) are mixed and brought to reaction temperature ( $220^{\circ}\text{C}$ ). The reactions take place in a tubular reactor (4 m diameter, 3 m length) which is adiabatically operated. The reactor is designed for the total conversion of reactants. Stream table of the process is given as Table 2. Fig. 3 shows mole fraction and temperature profiles along the reactor. The conversion of reactants into products is uniformly distributed along the reactor length and almost constant temperature should be remarked.

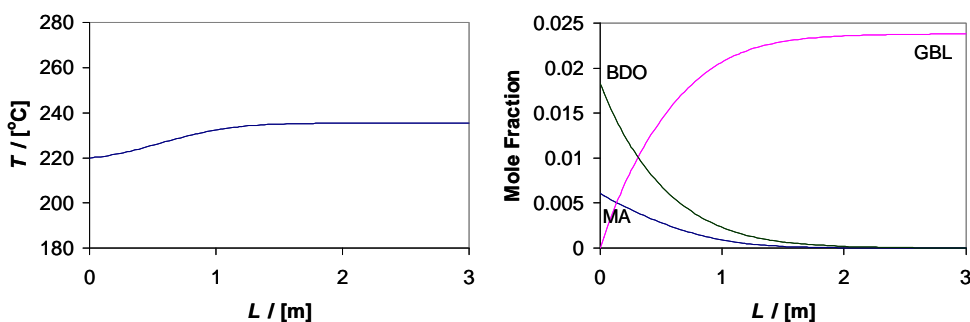


Fig. 3 Temperature and Molar Profile

Table 2

Stream Table (Heat Balance)								
	MA	BDO	GBL	H2REC	RIN	ROUT	SEPIN	WATER
Temperature (°C)	25	25	203	20	220	235	20	45
Pressure (bar)	1.5	1.5	1	1.2	1.5	1.5	1.2	1
Vapor Fraction	0	0	0	1	1	1	0	0
Mole Flow (kmol/hr)	20	60	79.84	3200	3310	3390	64.56	19.22
Mole Fraction								
Hydrogen	0	0	0	0.991	0.967	0.962	0	0
Water	0	0	0	0.009	0.009	0.014	0.228	0.996
MA	1	0	0	0	0.006	0	0.002	0
GBL	0	0	1	0	0	0.024	0.769	0.004
BDO	0	1	0	0	0.0018	0	0.001	0

The reactor outlet is cooled to 20 °C, and vapor – liquid separation is performed. The hydrogen is recycled. The amount of hydrogen generated by the reactions is withdrawn and can be stored and used for other purposes. As the complete conversion (> 99.5%) of reactants is achieved, there is no recycling of reactants simplifying technical difficulties. A high boiling point difference between water and GBL result in easier separation by distillation. GBL is obtained as a product at the rate of 79.8 kmol/h with high purity > 99.5%. In heat coupled system, the plant can be operated at much lower ratio, hydrogen : feed (BDO + MA) = 40:1 as compared to 100:1 in hydrogen coupling. Even at this low ratio, the temperature is under control.

#### 4. Parametric Sensitivity

The chemical reactor deserves a special discussion. To remove the risk of run-away in hydrogenation of maleic anhydride as an individual process a large excess of hydrogen to feed ratio (100 – 200: 1) is provided to the system. Despite this, the reaction is very difficult to control. The operation of the integrated reactor is simulated, at various process conditions, in order to emphasize the stability of reactor with reduced parametric sensitivity.

Fig. 4 and Fig. 5 show the effect of changing the reactor-inlet temperature and the hydrogen to feed ratio on the products mole fractions and temperature respectively.

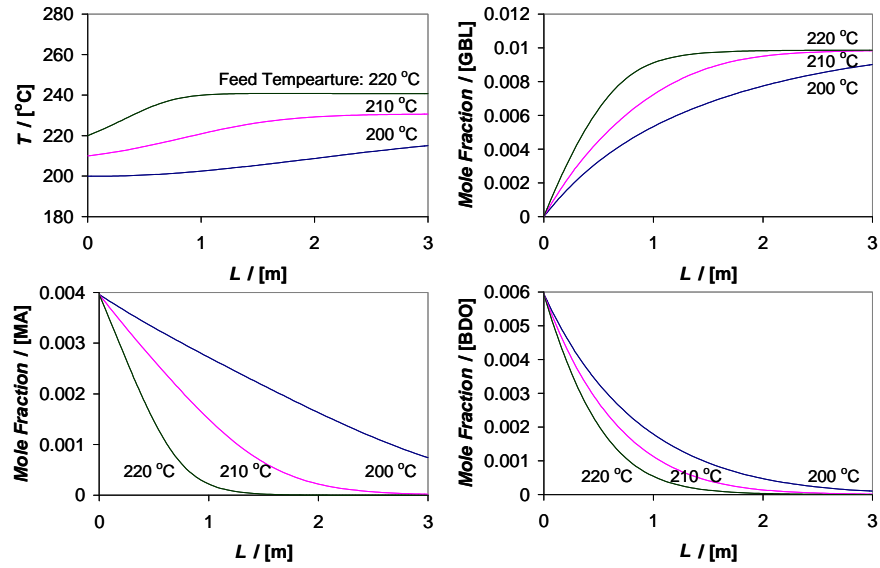


Fig. 4 Effect of Feed Temperature (Hydrogen Balance)

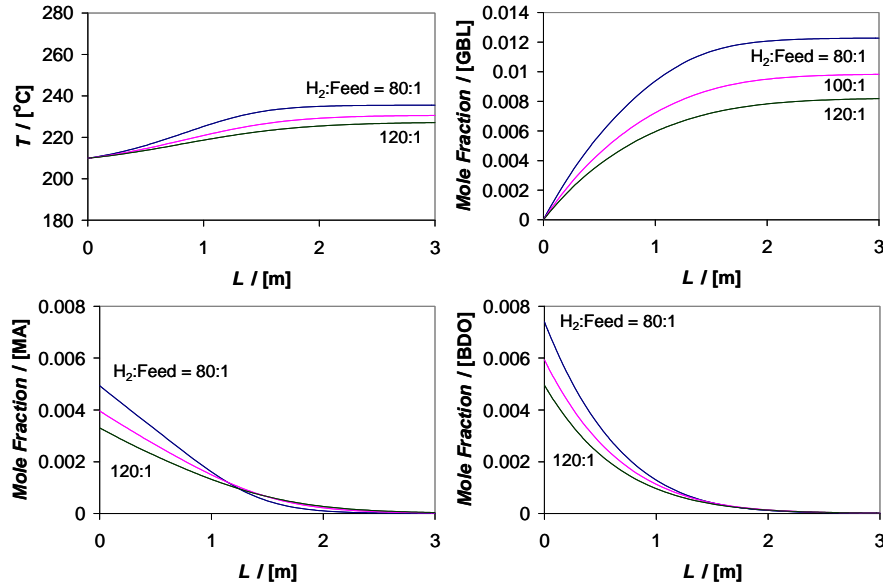


Fig. 5 Effect of Hydrogen to Feed Ratio (Hydrogen Balance)

Fig. 6 and 7 shows the effect of changing the reactor inlet feed temperature and hydrogen to feed ratio on molar and temperature profiles for the heat-balance setup. The reduced reactor sensitivity with respect to disturbances is observed.

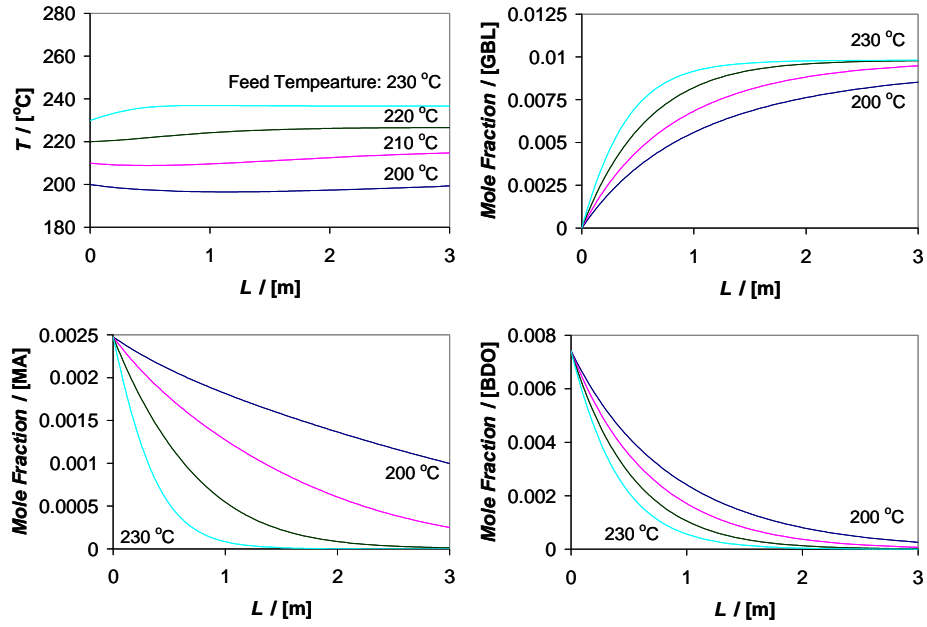


Fig. 6 Effect of Feed Temperature (Heat Balance)

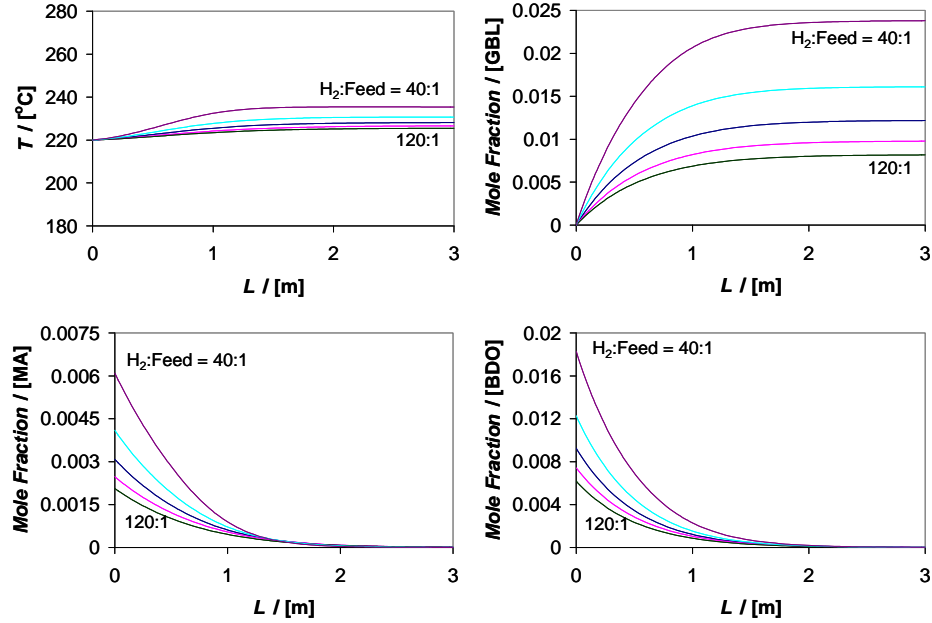


Fig. 7 Effect of Hydrogen to Feed Ratio (Heat Balance)



## 5. Plantwide Dynamics and Control

The plantwide control system fixes the flow rate of maleic anhydride, 1,4-butanediol and hydrogen at reactor inlet. Control of heat exchangers, two-phase separator and distillation column is standard. A dynamic model was built in Aspen Dynamics and flexibility in changing the production rate was investigated. For hydrogen-balance and heat-balance designs, starting from steady state, the MA and BDO feed rates were increased or decreased, as shown in Fig. 8. The change in feed rate is followed by change in production rate of GBL while purity remains the same.

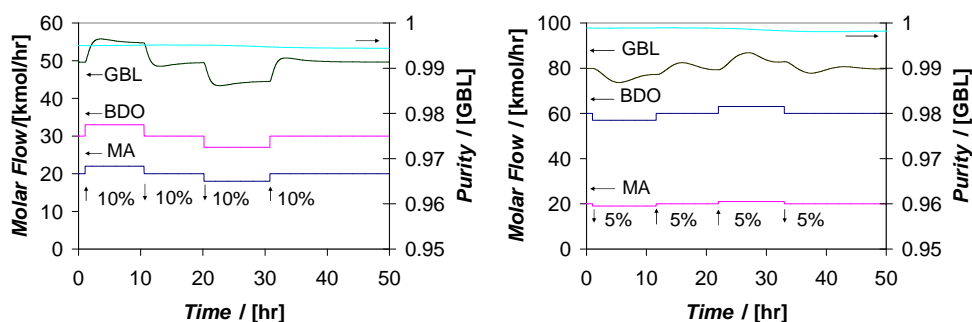


Fig. 8 Dynamic Simulation (Hydrogen Balance - left, Heat Balance - right)

## 6. Conclusions

The coupling of exothermic maleic anhydride hydrogenation with the endothermic 1,4-butanediol dehydrogenation leading to  $\gamma$ -butyrolactone can be achieved with overall reactants conversion exceeding 99.5% and product purity above 99%. The coupling can be done according to hydrogen balance or energy balance, the later one being preferred.

Compared to a conventional process, where the reactions are carried on in two separate reactors and energy is transferred from one reactor to another by means of a heat carrier, the coupled process offers several advantages:

- reaction coupling (energy balance) allows reduction of the hydrogen excess by at least a factor 2.5 (from 100-200 to 40).

- the reaction system is much simpler, namely one adiabatic reactor instead of two multi-tubular reactors with heating and cooling, respectively. There is no need of a heat carrier, and the hydrogen recycle system is much simpler.

The plant is controllable, allowing for changes in production rate while keeping high product purity.

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