

Effect of different feed strategies on integrated toluene-aniline production reactor

A. Javaid*, R. Ajaz

*Department of Chemical Engineering, Pakistan Institute of Engineering & Applied Sciences,
Nilore, 45650, Islamabad, Pakistan*

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Hydrogen is an important energy transporter and is widely used in hydrogenation reactions for the synthesis of various valuable chemicals. It can be obtained through dehydrogenation reactions and the acquired hydrogen can directly be utilized in hydrogenation reactions. As a result, external hydrogen supply is minimized which makes it an economical process. Technique of coupling exothermic and endothermic reactions in a single reactor is among the methods of process intensification. Simultaneous production of toluene and aniline in an integrated reactor has been found feasible, economical and controllable in our previous study. The scope of this research is to study the effect of different feed strategies for simultaneous production of aniline and toluene. Both reactions are carried out in an adiabatic reactor curtailing the requirement of heating or cooling and eliminating a large amount of hydrogen recycle needed to avoid reaction run-away. Using Aspen plus, alternative feed strategies for both the reactants are employed to find out the best possible strategy in terms of reactant conversion. Preeminent option found is to feed both reactants completely at the reactor inlet. The conversion of methyl-cyclohexane and nitrobenzene is 74% and 98%, respectively. The results achieved in this study can be correlated with relevant chemical processes.

Keywords: Design, Feed Strategy, Process Integration, Reaction Coupling, Aspen

INTRODUCTION

The idea of combining several processes in a single unit is not new. The process integration concept has started back in 1970's [1]. Coupling of exothermic and endothermic reactions is among the methods of process intensification for material and energy utilization. The heat produced by exothermic reactions is used to drive the endothermic reactions, improving thermal efficiency and increasing equilibrium conversion & reaction rate for reversible reactions [2]. Coupling could be hydrogenation with dehydrogenation, oxidation with reduction, or hydration with dehydration. Many researchers have studied the possibility of coupling of more than one reaction in a single unit. It resulted in a small-sized reactor with reduced complexity and energy savings as an additional benefit [3]. These energy savings combined with reduced reactor investment must overshadow the cost of required additional separation units [4].

Studying coupling of exothermic and endothermic reactions has been a field of interest for researchers for a while but the real intensity in this field is seen since 1994 [5, 6]. The study of simultaneous dehydrogenation and hydrogenation reactions are important as they have several advantages over individual reactions. Coupling reactions offer various advantages as: mild reaction environment, simpler operation, optimum hydrogen

usage, thermodynamic limitations shift, eco-friendliness and good quantitative yields [7]. On the other side, individual reactions have limitations and these limitations can be eliminated by combination of these categories of reactions. Owing to aspects listed above, coupling reactions have gained momentum and lot of research methodologies are in process of continuous development. Extensive reviews of different catalytic reactors used for coupling exothermic and endothermic reactions, particularly hydrogenation and dehydrogenation are provided elsewhere [8, 9].

Over the period, many researchers tried to carry out simultaneous reactions in a single reactor and found this intensification technique useful but their studies are limited to reactor only, more specifically for catalyst selection. In our previous studies [10-12] an integrated toluene-aniline plant is found feasible in terms of economy and controllability. The goal of this research is to find out the best feed strategy in terms of reactants (MCH and AN) conversion. Although in some studies coupled behavior is analyzed in a stand-alone integrated plant [13-16], there is no research regarding using alternative feed strategies either for maximizing product yield or to focus uniform temperature profile in the reactor. Hence, this study is an attempt to fill that gap.

Types of thermal reactors

The reactors used for coupling processes can be divided into three types: direct, regenerative and

* To whom all correspondence should be sent:
E-mail: ahteshamjavaid@hotmail.com

recuperative.

Direct coupling reactor. In this mode of coupling two or more reactions occur simultaneously in an identical reaction zone, where the material and energy are interchanged directly in the reaction mixture. However, there are some limitations to carry out direct coupling, e.g. the catalysts for both the reactions shall be in a similar temperature and pressure condition because both reactions are occurring simultaneously in the same catalyst bed. Direct coupled reactor is further classified into simultaneous direct coupling adiabatic reactor (SIMDCAR) which is made of uniformly mixed exothermic and endothermic catalysts favoring both the exothermic and the endothermic reaction, and sequential direct coupling adiabatic reactor (SEQDCAR) in which alternating exothermic and endothermic catalytic bed is used.

Regenerative coupling reactor. In a regenerative reactor, reactions are conducted in a single reaction zone but only one reaction is occurring at one time, so by storing and discharging cycles, energy and material are interchanged. It is generally suitable

for the integration of several process steps with the main advantages: direct heat supply and efficient heat recovery. They are well suited for weak exothermic reactions. Main drawbacks are the development of hot spots which can damage the catalyst and the reactor walls.

Recuperative coupling reactor. In this type of coupling the reactions are occurring simultaneously but are separated physically either by separation wall or membrane. The energy interchange is anticipated through the wall or membrane but material interchange is only possible by permeation through the membrane. These types of reactors can be operated co-currently or counter-currently.

The detailed comparison among different schemes of coupling and guidelines regarding effective coupling for better results and linear temperature profiles are provided elsewhere [17]. Types of coupling reactors are shown in Fig. 1.

This study and outcomes are only based on coupling of hydrogenation and dehydrogenation reactions occurring simultaneously in a directly coupled single-tube adiabatic reactor.

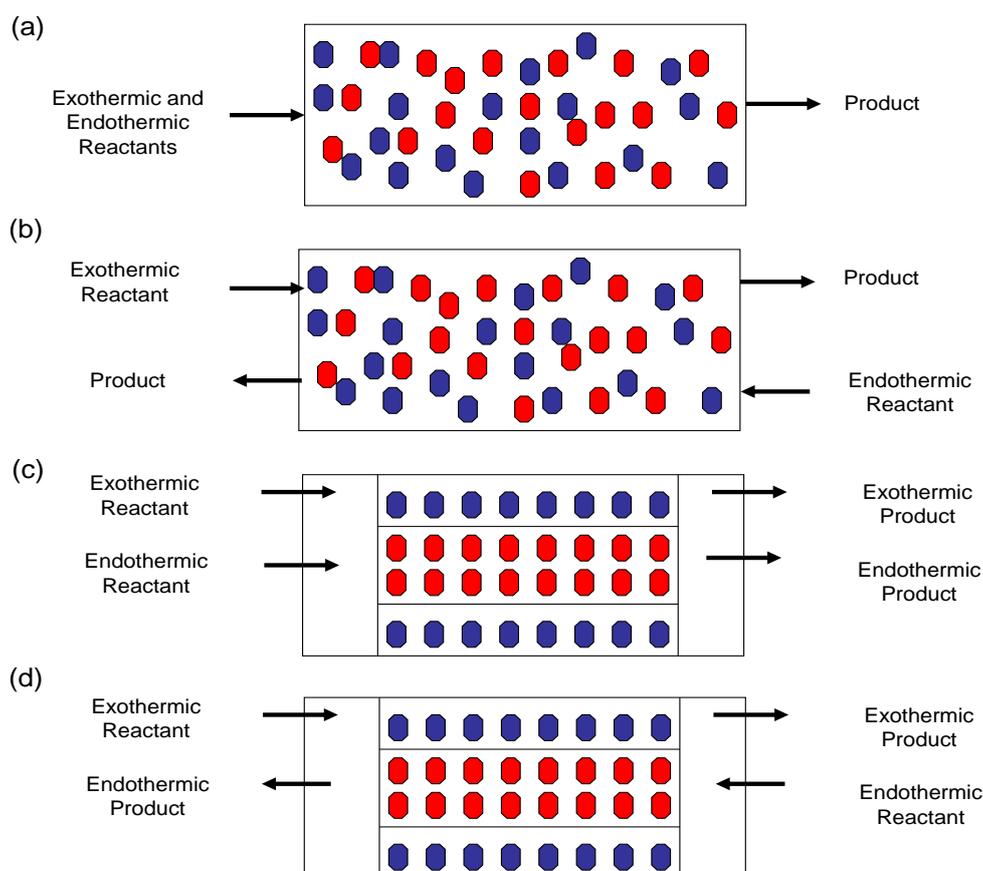
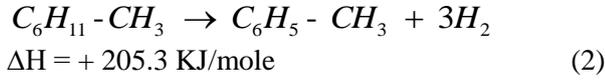
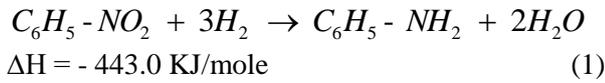


Figure 1. Reactors for coupling of reactions: (a) direct (b) regenerative (c & d) recuperative co- and counter-current

EXPERIMENTAL

Integrated toluene-aniline system

Aniline (AN) is produced industrially by hydrogenation of nitrobenzene (NB). The reaction is highly exothermic so a multi-tubular reactor is used. In spite of the large heat transfer area, still excess hydrogen is required up to 100:1 to keep temperature under control. Moreover, the recycling of hydrogen adds additional costs. Endothermic dehydrogenation of methyl-cyclohexane (MCH) to toluene (TOL) is a process which requires a large amount of heat and results in increased total annual cost of the plant. Both reactions are given in Eqns. 1 and 2.



Design procedure

Reactor performance is specified as reactant conversion in Aspen Plus [18]. It allows preliminary mass balance which gives the reactor-inlet stream and consequently reactor diameter can be calculated. Using knowledge of reaction kinetics, the reactor length can be found. The following kinetic expressions are used in the simulation:

Nitrobenzene hydrogenation (copper-nickel catalyst) [19]:

$$r_1 = k \cdot p_{\text{NB}}^{0.5} \cdot p_{\text{H}_2}^{0.5} \quad (3)$$

$$k = 0.114 \exp\left(-\frac{8323}{T}\right) \text{ kmol} \times \text{m}^{-3} \times \text{s}^{-1} \times \text{Pa}^{-1} \quad (4)$$

MCH dehydrogenation (platinum on alumina catalyst) [20]:

$$r_1 = k_1 \cdot p_{\text{MCH}} \quad (5)$$

$$k_1 = 3.07 \times 10^{13} \exp\left(\frac{-26539}{T}\right) \text{ kmol} \times \text{m}^{-3} \times \text{s}^{-1} \times \text{Pa}^{-1} \quad (6)$$

Integrated reactor

To assess the feasibility of simultaneously performing MCH dehydrogenation and NB hydrogenation, an adiabatic reactor having 4 m length and 1.5 m diameter was considered. Catalysts were mixed and used in equal proportions. Ratio between the catalysts can be changed to tune the reaction rates. Peng-Robinson thermodynamic model was used for simulation. Reactants were mixed and fed to reactor; MCH 60 kmol/h, NB 20 kmol/h, and H₂ 100 kmol/h at 1.5 bars and 300 °C. The ratio between reactants was chosen to approximately match the theoretical value for which heats of reactions balance each other. The conversion of MCH to toluene and of nitrobenzene to aniline was 74% and 98%, respectively. Temperatures and molar profiles along the reactor length are given in Fig. 2. The uniform temperature distribution resists the catalyst deactivation.

Due to limitation of simulation software the feed cannot be introduced at different length intervals or sections of the reactor, so the reactor of 4-m length was disintegrated into 4 reactors each having length of 1 m. By disintegrating, the effect of different feed strategies on the temperature and molar profiles will be more prominent. In this research, two case studies were considered where behavior of both the reactants was studied by using alternate feed strategies for nitrobenzene and methyl-cyclohexane.

Case 1. Alternative feed strategies for NB in the coupled system

In the first scenario the total feed of NB (20 kmol/h) was divided equally (50%) in the first two reactors at 10 kmol/h in each reactor. In the second scenario, the feed was divided equally (33%) in the first three reactors at 6.67 kmol/h. In the third scenario, the feed was divided equally (25%) in all four reactors at 5 kmol/h. Schematic diagram of the latter scenario is given in Fig. 3.

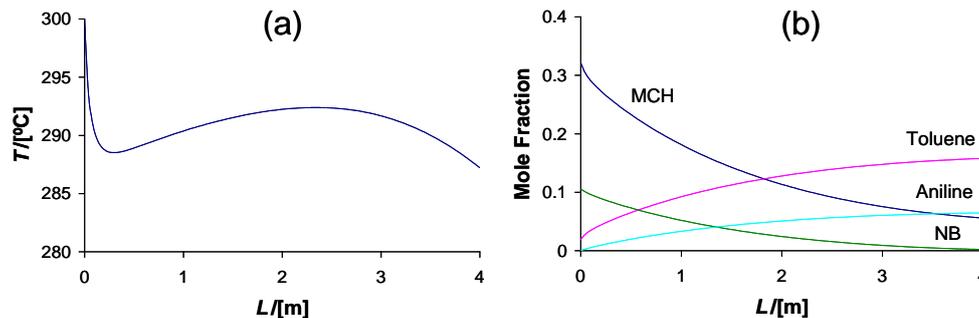


Figure 2. Reactor profiles: (a) Temperature (b) Molar

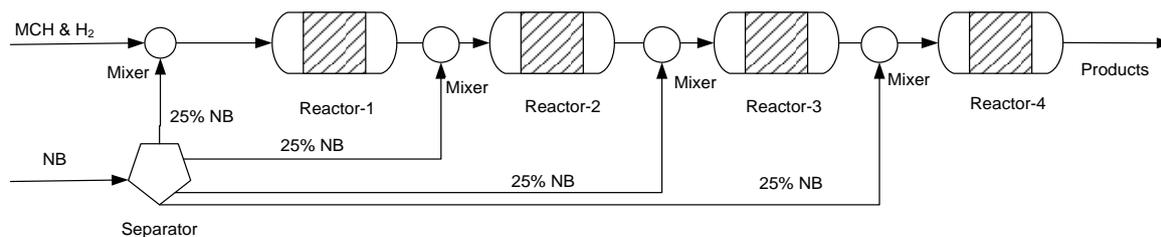


Figure 3. Alternative feed strategies for NB (25%)

The stream coming out of reactor-4 consisted of products (toluene, aniline, water, hydrogen) and un-reacted reactants (methyl-cyclohexane and nitrobenzene), the components in the mixture were analyzed with the help of modern analytical (quantitative and qualitative) methods prior to its separation. The basis of separation was the miscibility and difference in boiling points. Hydrogen and water were separated from the mixture in a vapor-liq-liq separator and two distillation columns were required to separate the two organic phases. Toluene and aniline were taken out as products (required production rate & purity) while un-reacted MCH and hydrogen were recycled into the system. Details of the separation section in

an integrated plant are provided in previous studies [10-12].

Case 2. Alternative feed strategies for MCH in the coupled system

On the similar lines as in NB feed, the effect of different feed strategies for MCH was also studied. In the first scenario the total feed of MCH (60 kmol/h) was divided equally (50%) in the first two reactors at 30 kmol/h in each reactor. In the second scenario, the feed was divided equally (33%) in the first three reactors at 20 kmol/h. In the third scenario, the feed was divided equally (25%) in all four reactors at 15 kmol/h. Schematic diagram for the latter scenario is provided in Fig. 4.

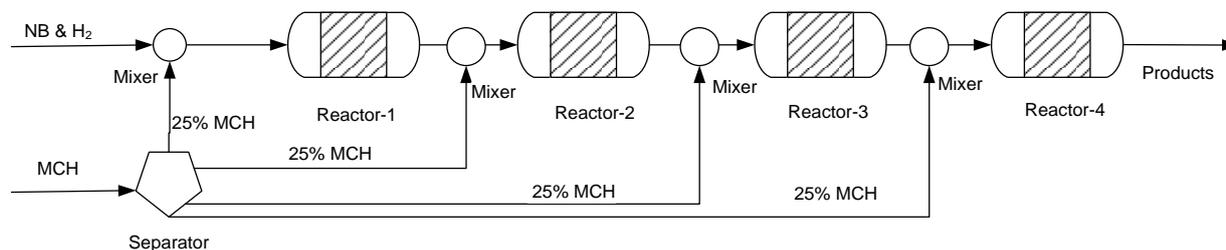


Figure 4. Alternative feed strategies for MCH (25%)

Table I. Comparison b/w NB feed flow strategies

Description/NB Feed Strategy	1	2	3	4
	100%	50%	33%	25%
Temperature R_{out} (°C)	286.4	289.8	292	292.8
Pressure (bar)	1.5	1.5	1.5	1.5
Feed (kmol/h)				
<i>MCH</i>	60	60	60	60
H_2	100	100	100	100
<i>NB</i>	20	20	20	20
Product (kmol/h)				
<i>MCH</i>	15.53	17.51	20.63	25.39
<i>TOL</i>	44.46	42.48	39.37	34.60
H_2	174.52	170.71	165.31	157.42
<i>NB</i>	0.37	1.08	2.40	4.53
<i>AN</i>	19.63	18.91	17.60	15.46
H_2O	39.25	37.82	35.20	30.93
Conversion (%)				
<i>MCH</i>	74	70.80	65.61	57.67
<i>NB</i>	98	94.57	88	77.32

RESULTS AND DISCUSSION

Case 1

In the first scenario, when feed is divided in first two reactors, the temperature sharply decreased from 300 °C to 278 °C in the first quarter of the reactor due to the 6:1 (MCH: NB) reactants ratio at the inlet. At the start of the second quarter a sudden increase in temperature is due to injection of nitrobenzene (10 kmol/h) leading to exothermic reaction. Once heats of both reactions started balancing each other the temperature profile was almost linear in the second half of the reactor. Similar effect can be observed in molar profiles. In the second scenario, when feed was divided in the first three reactors, again the temperature sharply decreased from 300 °C to 270 °C in the first quarter of the reactor due to the high reactants ratio 9:1 (endo: exo) at the reactor inlet. Sharp increase in

the second and third quarter was observed when nitrobenzene entered in the reactor. Linear temperature profile was observed in the last quarter of the reactor. In the third scenario, the feed was divided between all reactors. As the reactants ratio at the reactor inlet was 12:1 so due to the endothermic reaction the temperature sharply decreased from 300 °C to 265 °C in the first quarter of the reactor. As noted in previous scenarios a sharp increase in temperature was observed due to hydrogenation reaction when nitrobenzene was periodically introduced into the reactor.

Comparison between different feed strategies based on NB flow in the reactor is given in Table 1. The temperature and molar profiles of scenarios 1, 2 and 3 are shown in Fig. 5 (top), (center) and (bottom), respectively.

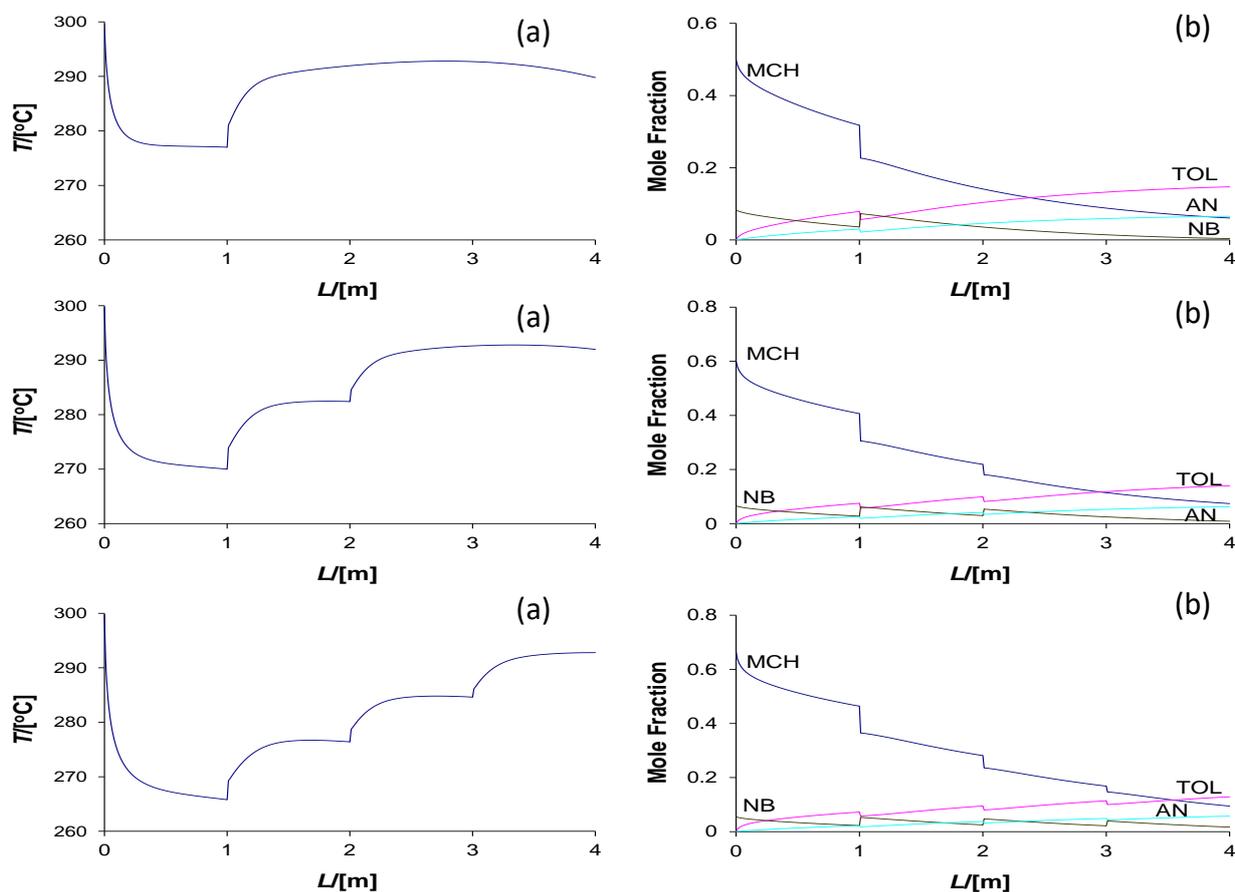


Figure 5. (a) Temperature, (b) Molar profiles (Top) 50% of NB is fed in first two reactors, (Center) 33% of NB in three reactors, (Bottom) 25% of NB in four reactors

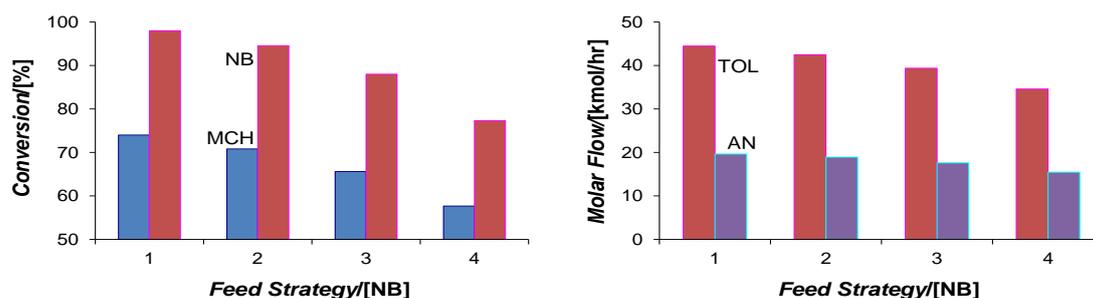


Figure 6. Comparison b/w NB feed flow strategies

It is evident from the results given in Fig. 6 that the conversion of MCH and NB decreases from 74% to 57% and from 98% to 77%, respectively, as NB feed flow is disintegrated.

Case 2

In the first scenario, when feed was divided in the first two reactors, the temperature increased up to 350 °C by the end of the first quarter of the reactor. As more MCH entered in the system the temperature profile started becoming linear when the heats of reaction started balancing each other. Maximum production of toluene was achieved in the first quarter and then conversion of both reactants was smooth along the reactor length. In the second scenario, MCH to NB ratio was (1:1) so due to the highly exothermic hydrogenation reaction a step-wise increase in temperature was observed and the temperature shot up to 690 °C. Similar behavior was observed in the third scenario where the highly exothermic reaction increased the temperature up to 780 °C and then the temperature decreased along the reactor length. In the second and third scenarios maximum conversion of reactants occurred in the first part of the reactor due to improper reactants ratio. In addition to the difficulty to control the reactor conditions sudden high temperature rise will cause damage to the catalyst. The temperature and molar profiles of all scenarios are shown in Fig. 7 (top), (center) and (bottom), respectively. Comparison between different feed strategies based on conversion is given in Table 2. From the results presented in Fig. 8, conversion of MCH to TOL and NB to AN slightly increased from 74% to 78% and 98% to 100% respectively, as MCH feed flow was disintegrated. On the other hand, as the total

reactants conversion was completed in the first quarter of the reactor (1 m), so a sharp increase in temperature led to hot spotting and catalyst deactivation.

It is evident from the results given in Fig. 8 that the conversion of MCH and NB decreases from 74% to 57% and from 98% to 77%, respectively, as the NB feed flow is disintegrated. In this work, four different possible feed strategies were compared to figure out the best strategy in terms of product yield. From all presented data it is clear that to maximize reactants conversion, both reactants should be fed completely together at the first reactor inlet. Linear and controlled temperature profiles were also achieved as an additional benefit which reduces hot spots and resists catalyst deactivation. The results achieved in this study may replicate in chemical processes of practical relevance.

CONCLUSION

Coupling exothermic nitrobenzene hydrogenation with endothermic MCH dehydrogenation is feasible with benefits of simpler chemical reactor, minimum heating/cooling requirement and direct hydrogen utilization which reduce hydrogen recycling cost. After analyzing four different possible feed strategies for each case (nitrobenzene and methyl-cyclohexane), the best strategy found in terms of product yield is to feed both the reactants completely together at the first reactor inlet. The conversion was 74% for MCH dehydrogenation and 98% for NB hydrogenation. Linear temperature profile which reduces hot spots and resists catalyst deactivation was also achieved as an additional benefit.

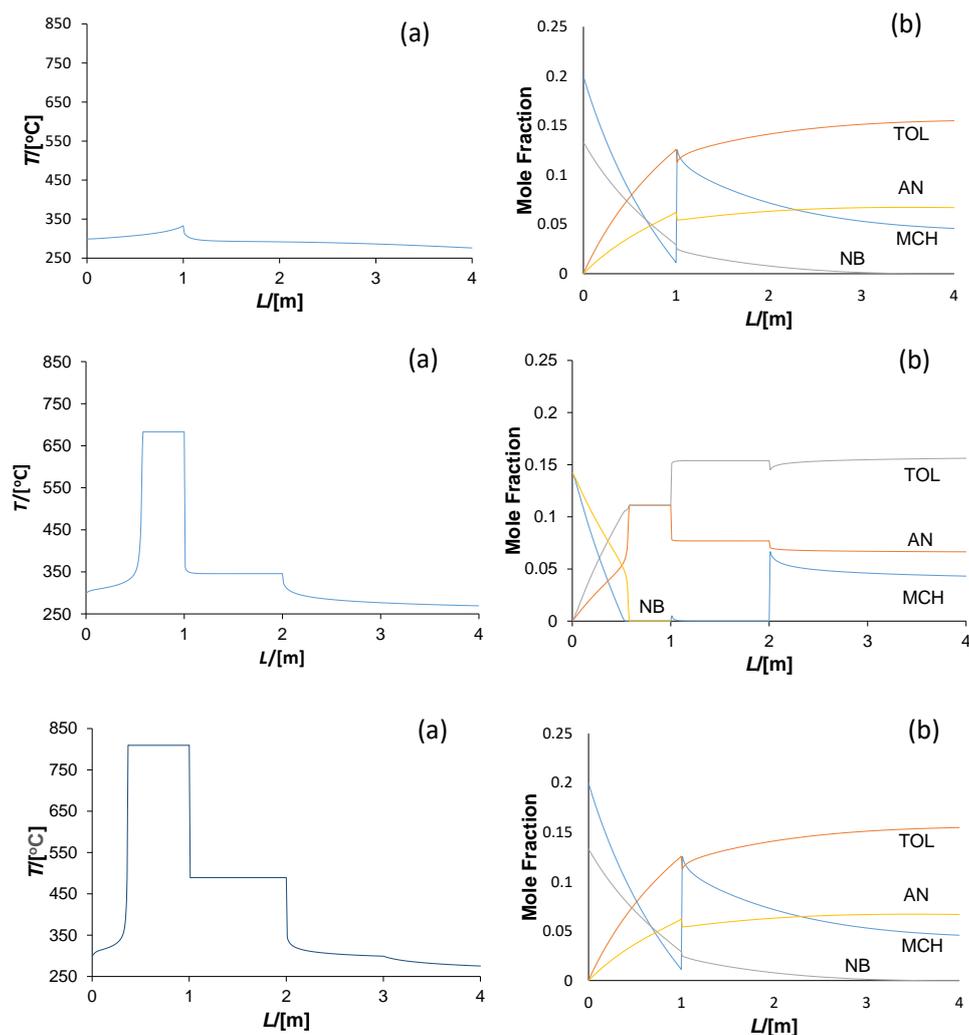


Figure 7. (a) Temperature, (b) Molar profiles (Top) 50% of MCH is fed in first two reactors, (Center) 33% of MCH in three reactors, (Bottom) 25% of MCH in four reactors

Table 2. Comparison b/w MCH feed flow strategies

Description/MCH Feed Strategy	1	2	3	4
	100%	50%	33%	25%
Temperature R_{out} ($^{\circ}\text{C}$)	286.4	276.2	269.4	275.3
Pressure (bar)	1.5	1.5	1.5	1.5
Feed (kmol/h)				
<i>MCH</i>	60	60	60	60
H_2	100	100	100	100
<i>NB</i>	20	20	20	20
Product (kmol/h)				
<i>MCH</i>	15.533	13.709	13.006	13.622
<i>TOL</i>	44.467	46.209	46.995	46.378
H_2	174.519	178.865	180.977	179.129
<i>NB</i>	0.373	--	--	--
<i>AN</i>	19.627	20	20	20
H_2O	39.255	40	40	40
Conversion (%)				
<i>MCH</i>	74	77	78.32	77.30
<i>NB</i>	98	100	100	100

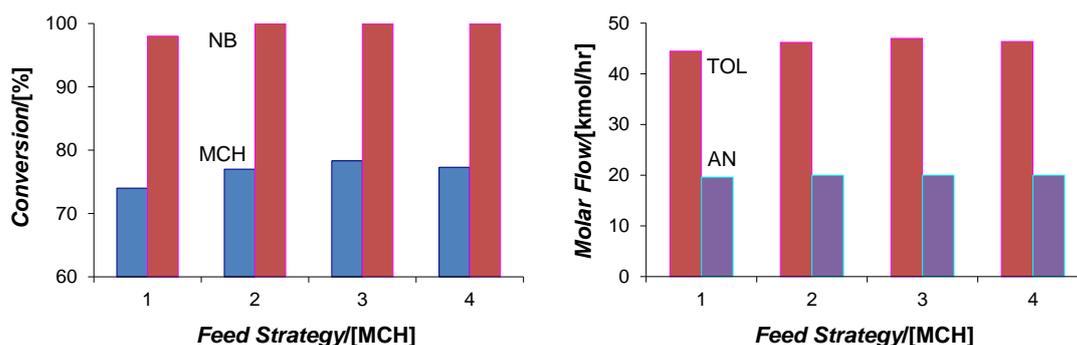


Figure 8. Comparison b/w MCH feed flow strategies

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