

Mathematical Modeling of Thermally Coupled Cyclohexane Dehydrogenation and Nitrobenzene Hydrogenation Reactors

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ARTICLE INFO	ABSTRACT
<p>Article History: Received: 28 January 2022 Revised: 06 September 2022 Accepted: 11 September 2022</p> <p>Article type: Research</p> <p>Keywords: Cyclohexane, Dehydrogenation, Nitrobenzene, Thermally Coupled Reactor, Modeling</p>	<p>In this study, a mathematical model is developed for a unique multi-tubular thermally coupled reactor in steady-state. The cyclohexane dehydrogenation procedure in the inner tube and the nitrobenzene to aniline hydrogenation reaction in the outer tube both occur in the aforementioned thermally coupled reactor. This research aims to utilize the heat produced by the exothermic process rather than heat-supply devices like heaters and furnaces. Therefore, the proposed configuration acquires a remarkable reduction in energy consumption. Besides, the required hydrogen is provided for the nitrobenzene's hydrogenation reaction to aniline by the dehydrogenation reaction of cyclohexane in the same reactor. Furthermore, compared to conventional reactors that operate in the same conditions as the thermally coupled reactor, better efficiency is attained in the suggested design depending on the heat transfer across the exothermic and endothermic sides of the reactor.</p>

Introduction

Cyclohexane is a comparatively stable cycloalkane observed in crude oil at negligible concentrations. This cycloparaffin is a colorless, flammable liquid broadly used as an intermediate in nylon production. Almost all cyclohexane produced commercially is employed in producing adipic acid and caprolactam, precursors to nylon [1]. A minor portion of cyclohexane is consumed in insignificant uses, such as polymer reaction diluents and solvents. The benzene hydrogenation process mainly produces cyclohexane. Hydrogen is a contaminant-free fuel and an appropriate replacement for the common environmental pollutant energy sources such as fossil fuels. The production process of hydrogen employs various techniques, including natural gas reforming, partial oxidation of fossil fuels, and water electrolysis [2, 3]. Hydrogen is not yet considered an ideal replacement for contaminant fuels on the industrial scale since the methods mentioned above are costly, and hydrogen must be transported and stored at a specific temperature and pressure [4, 5].

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In the current study, the produces a significant amount of hydrogen and benzene without releasing greenhouse gases according to the following endothermic catalytic reaction on the Pt/Al₂O₃ catalyst [6, 7].



Benzene is an aromatic hydrocarbon extensively utilized to produce rubbers, nylons, and polystyrenes. Moreover, it is a well-known chemical substance for increasing the octane number of fuels [8, 9].

Akamatsu et al. [10] improved the cyclohexane dehydrogenation membrane reactors by employing membranes of the amorphous silica type in the pressure range of 1-8 atm. Their proposed membranes resulted in higher conversions than equilibrium. In 2004, Jeong et al. [11] created a mathematical model centered on an isothermal procedure using plug flow to assess the efficiency of a membrane reactor for cyclohexane dehydrogenation. Consequently, they observed a respectable level of agreement between the simulated findings and the empirical data. In 2017, Wang et al. investigated cyclohexane dehydrogenation in a bulb reactor by considering volume expansion on a single platinum crystal. They derived a kinetic model based on the Hougen–Watson approach and utilized Co-oxidation to ensure the validity of the proposed kinetic model [2].

An important industrial process used to produce aniline for the plastics industry is the catalytic hydrogenation of nitrobenzene. Commercially, the reaction is conducted in the gas phase over a catalyst made of nickel or copper. The following reaction describes how to hydrogenate nitrobenzene, which is mostly used to make aniline, in the gas or liquid phase utilizing supported metal catalysts and organic solvents including acetone, alcohols, ethyl acetate, benzene, or aqueous acidic solutions [12-14].



As a precursor to aniline, benzene is used to make nitrobenzene, an important organic chemical. A colorless to pale yellow oily liquid, nitrobenzene has an aroma reminiscent of bitter almonds or shoe polish. Additionally, aniline, a crucial chemical intermediary needed in the production of polyurethane, is synthesized using more than 95% of the nitrobenzene that is produced. Additionally, nitrobenzene is employed in the refinement of petroleum, as a mediator in the synthesis of other organic compounds, such as acetaminophen, and as a solvent required for the production of cellulose ethers and acetates [15, 16].

The simplest aromatic amine is aniline, an organic chemical. It is also a valuable commodity chemical for industry and a flexible precursor for the synthesis of fine chemicals. Its main use is in the production of compounds used in industry, such as dyes and polyurethane precursors [17]. There are two processes in the manufacturing of industrial aniline. To create nitrobenzene, benzene is first nitrated at 50 to 60 °C using strong nitric acid and sulfuric acid. After that, the nitrobenzene is hydrogenated with metal catalysts (usually at 200–300 °C). Aniline, a hazardous aromatic amine, is a common industrial chemical used in the production of rubber chemicals, herbicides, explosives, fungicides, varnishes, resins, fragrances, isocyanates, pigments, and dyes [13, 18, 19].

Abo-Ghander et al. [20] simulated the reactions of dehydrogenation of ethylene benzene and hydrogenation of nitrobenzene in a heterogeneous coupled membrane reactor given the Fick's model of diffusion within the catalyst pellets. After examining the results of the homogeneous model with the heterogeneous model, it was found that the homogeneous model evaluated the performance by 5-15% of the actual yield. Liu et al. developed a double-pipe catalytic membrane micro-reactor for solid-liquid-gas reaction. Experimental results illustrated the high conversion rate of nitrobenzene over a 30-hour continuous operation. The effects of the flow

rate and concentration of input nitrobenzene were also studied in their work. Sufficient hydrogen improved the reaction and increased nitrobenzene conversion and aniline production. The higher concentration of nitrobenzene in the inlet increased the reaction rate and caused the catalyst's poisoning. Finally, according to the results, the catalytic membrane micro-reactor for G-L-S reactors was useful, especially for catalytic reactions [16]. Yadav et al. studied the synthesis of azobenzene produced from aniline oxidation, which is also a by-product of the nitrobenzene hydrogenation reaction to aniline. They reviewed the effect of the parameters, including catalyst value, hydrogen pressure, nitrobenzene concentration, and temperature; they eventually proposed a suitable mechanism and kinetic for the reaction [21]. Turáková et al. examined nitrobenzene hydrogenation in a methanol solution on the Pd/C catalyst at a 2-4 MPa pressure and 30-70 degrees Celsius temperature in a batch reactor on a laboratory scale. A zero-degree reaction was observed at a hydrogen pressure above 2 MPa. The activation energy was 35 ± 1 kJ mol⁻¹; ultimately, they offered a brand-new method of heterogeneous hydrogenation of nitrobenzene [22].

Thermal coupling of appropriate reactions makes it possible for the produced heat to be moved to the endothermic side from the exothermic side, leading to the elimination of the cooling and heating equipment in the process [23-25]. Hence, this investigation targets to simulate a multifunctional thermally coupled reactor where the cyclohexane dehydrogenation to benzene endothermic reactions and nitrobenzene's hydrogenation reaction to aniline coincide. In addition to reducing energy consumption and providing the endothermic reactions' heat demand, the proposed process provides all the needed hydrogen for the aniline synthesis. Consequently, it reduces the production, storage, and transportation costs of hydrogen.

In the studies that are done before, thermal coupling processes were mainly done based on the auto-thermal procedure. The endothermic reaction's need for heat is met by the exothermic reaction's produced heat in the thermal coupling process. We may use extremely exothermic processes in thermally coupled reactors and pair them with the proper endothermic reactions to provide suitable temperature profiles and conversions, whereas mild to moderately exothermic reactions can primarily be exploited in auto-thermal reactors [26]. When the processes on the reactor's exothermic and endothermic sides are both reversible, thermal coupling can also speed up the reaction rate and change the reactor's equilibrium. Another benefit of these reactors over auto-thermal reactors is the simultaneous synthesis of several distinct products along with the prevention of the development of undesirable products throughout the procedure [27-29].

In 2007, Patel and Sunol developed a mathematical model which consisted of 22 coupled equations for a membrane reactor, including three channels in which methane combustion was thermally coupled with methane steam reforming. Moreover, they studied the performance of the reactor under different operating conditions [30]. In 2017, Chen et al. proposed a new method for hydrogen production: a microreactor was used to perform the thermal coupling of methane steam reforming and methane combustion processes. Besides, they investigated the best process parameters to reach the optimum performance of the reactor [31]. Afterward, Javaid et al. proposed an adiabatic reactor based on the direct coupling method for toluene and aniline simultaneous production. Their coupled process reduced the required hydrogen and the total annual cost of the process [32].

Process Description

Fig. 1 depicts the suggested plant's schematic diagram where cyclohexane and nitrobenzene are fed to the thermally coupled reactor. As illustrated on the hydrogenation side, the feed flow, including nitrobenzene and hydrogen, first enters a heater to reach the required reaction temperature. After entrance to the inner tube of the reactor (Fig. 2), a product flow consisting of aniline and unreacted H₂ and nitrobenzene is achieved. Afterward, the condenser cools down the flow, and aniline can be collected as the final product.

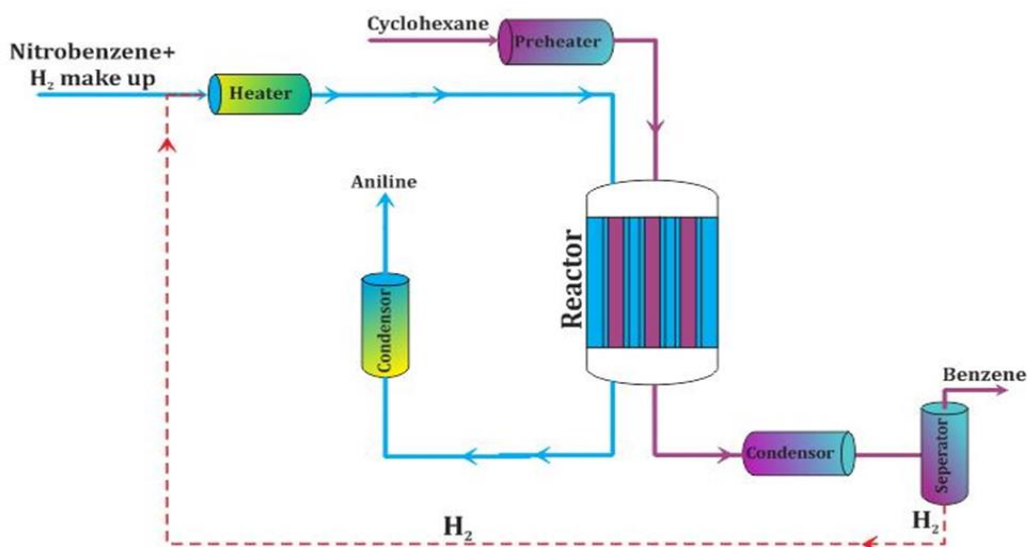


Fig. 1. The thermal coupling procedure's schematic diagram

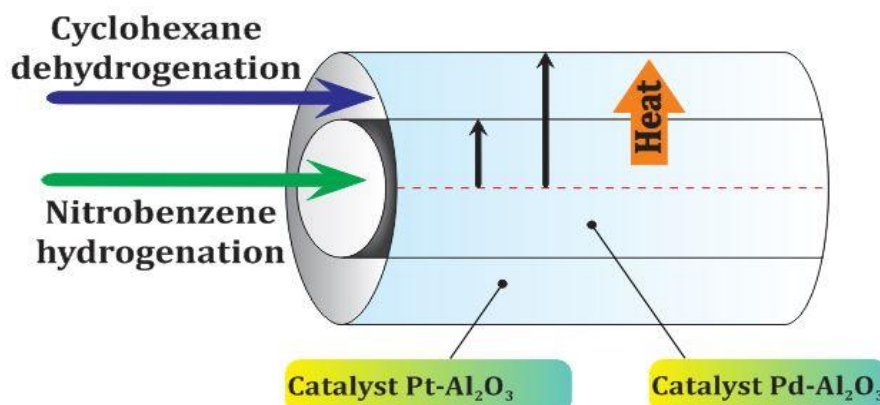


Fig. 2. The thermally coupled reactor's conceptual diagram

Moreover, cyclohexane flows through the outer tube of the reactor after preheating, according to Fig. 2. Then, the product flow, which is a combination of hydrogen and benzene, is sent to the condenser to be cooled down. Subsequently, hydrogen from benzene is separated and sent to the nitrobenzene hydrogenation side as the feed. The suggested thermally coupled reactor is seen in detail in Fig. 2, where the exothermic nitrobenzene hydrogenation process in the reactor's inner tube supplies the necessary heat for the endothermic cyclohexane dehydrogenation reaction. The operational circumstances and features of the thermally coupled reactor have been illustrated in Table 1 [11, 20, 33].

Table 1. Operating circumstances and features of the thermally coupled reactor

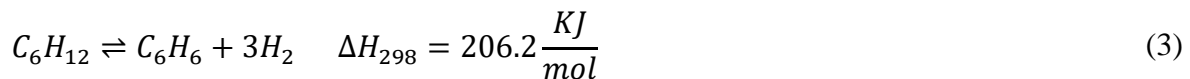
Parameter	Value
The Inner Tube (Cyclohexane Dehydrogenation)	
catalyst density, kg m ⁻³	2161.6
Catalyst	Pt/Al ₂ O ₃
bed porosity	0.39
catalyst particle's diameter, mm	3.55
C ₆ H ₁₂	0.90

feed composition, mole fraction	
inlet temperature, K	523
Ar	0.10
total feed molar flow rate, kmol h ⁻¹	1191
inlet pressure, Pa	10 ⁵
inner tube diameter, m	0.41
The Outer Tube (Nitrobenzene Hydrogenation)	
Catalyst	Pd/Al ₂ O ₃
catalyst density, kg m ⁻³	1400
catalyst particle's diameter, mm	4.7
bed porosity	0.40
feed composition, mole fraction	
H ₂	0.75
Nitrobenzene	0.25
inlet pressure, Pa	1.1×10 ⁵
inlet temperature, K	860
total feed molar flow rate, kmol h ⁻¹	2075.3
outer tube diameter, m	0.96

Reaction Kinetics

Cyclohexane Dehydrogenation

Cyclohexane can be dehydrogenated through the following equilibrium reaction [34]:



The rate of dehydrogenation reaction, which causes the production of benzene and hydrogen, can be calculated as below:

$$r_c = \frac{-k \left(\frac{K_P P_C}{P_{H_2}^3} - P_B \right)}{1 + \left(\frac{K_B K_P P_C}{P_{H_2}^3} \right)} \quad (4)$$

where the equilibrium constants as functions of temperature are obtained through the following equations [35]:

$$k = 0.221 \exp\left(\frac{-4270}{T}\right) \quad (5)$$

$$K_B = 2.03 \times 10^{-10} \exp\left(\frac{6.270}{T}\right) \quad (6)$$

$$K_P = 4.89 \times 10^{35} \exp\left(\frac{3.190}{T}\right) \quad (7)$$

Nitrobenzene Hydrogenation

The nitrobenzene hydrogenation reaction occurs at the exothermic side of the reactor, i.e., in the inner tube of the reactor, which is described by the following equation:



The rate equation for this reaction is provided by Amon [36]:



$$r = \frac{k' K_{NB} K_{H_2} P_{NB} P_{H_2}^5}{(1 + K_{NB} P_{NB} + K_{H_2} P_{H_2}^5)^2} \quad (9)$$

Table 2 demonstrates the equilibrium constants (K_I), reaction rate constant (K'), standard reaction heat (ΔH_{298k}), and the activation energy (E).

Table 2. Kinetic parameters for hydrogenation of nitrobenzene process

$k = A' \exp\left(B' - \frac{E'}{1} \cdot 8 T\right)$	A'	B'	E'	ΔH_{298k}
k'	0.186	0	10	-443000
K_{H_2}	4.427×10^{-3}	0	0	–
K_{NB}	1.51×10^{-5}	0	0	–

Mathematical Model

A trustworthy way to explain system behavior, figure out outlet parameters, and forecast system circumstances are through mathematical modeling. Mathematical modeling is the process of describing a system using mathematical equations. To characterize, predict, and optimize the operating circumstances and develop an appropriate controller, it is crucial to identify a system's key properties. Process design, process safety, process control, environmental impact assessments, operational training simulators, etc. are some main applications for model equations. Different types of mathematical model equations could be necessary depending on the application field. The mathematical modeling approach also includes experimental testing, analysis, and numerical simulation. General rules and constitutive relations are needed for the construction of mathematical models. The conservation or balance equations for mass, momentum, and energy are the fundamental laws [37, 38].

In the current investigation, a thermally coupled reactor has been modeled where nitrobenzene hydrogenation and cyclohexane dehydrogenation occur. The model is employed depending on the steady-state condition where the feeds flow only in the axial direction through the homogenous beds with variable physical properties. Finally, the equations are solved using the 4th-order Runge–Kutta technique. Table 3 lists the mass and energy balance equations for the exothermic and endothermic sides of the reactor.

Table 3. Balances of mass and energy as well as the coupled reactor's physical characteristics

Mass Balance	$\frac{dF_i}{dZ} = \eta R A_c v_i$	(10)
	$\frac{dT^{Exo}}{dZ} = \frac{\left((-\Delta H^{Exo} \times R_{Exo}) - \left(\frac{2U(T^{Exo} - T^{Endo})}{r_i} \right) \right) (M^{Exo} \times A_c^{Exo})}{m^{Exo} \times C_{p_{mix}}^{Exo}}$	(11)
Energy Balance	$\frac{dT^{Endo}}{dZ} = \frac{\left((-\Delta H^{Endo} \times R_{Endo}) + \left(\frac{2U(T^{Exo} - T^{Endo})}{r_i} \right) \right) (M^{Endo} \times A_c^{Endo})}{m^{Endo} \times C_{p_{mix}}^{Endo}}$	(12)
Overall Heat Transfer Coefficient	$\frac{1}{U} = \left(\frac{1}{h_i} + \frac{A_i \ln(D_o/D_i)}{2\pi L K_w} + \frac{A_i}{A_o} \times \frac{1}{h_o} \right)$	(13)
Coefficient of Heat Transfer across the Gas Phase and the Reactor Wall	$h = 4.21 \left(\frac{K_f}{d_p} + \frac{\rho u_g d_p}{\mu} \right)^{0.365}$	(14)
Specific Heats for Pure Components	$C_p^0 = C_1 + C_2 \left[\frac{\frac{C_3}{T}}{\sinh\left(\frac{C_3}{T}\right)} \right]^2 + C_4 \left[\frac{\frac{C_5}{T}}{\cosh\left(\frac{C_5}{T}\right)} \right]^2$	(15)
The Viscosity of Reaction Mixtures	$\mu = \frac{C_1 T^{C_2}}{1 + C_3/T + C_4/T^2}$	(16)
Pressure Drop	$\frac{dP}{dz} = \frac{150\mu(1-\varepsilon)^2}{\varphi_s^2 d_p^3 \varepsilon^3} u + \frac{1.75\rho(1-\varepsilon)}{\varphi_s d_p \varepsilon^3} u^2$	(17)

Model Validation

A model is a representation that attempts to approximate reality, and a mathematical model is one type of representation. In the process of constructing a model, we transform our real-world situation into a comparable, interpretable mathematical problem. The models we deal with in the process engineering area are fundamentally mathematical. In the form of equations, they attempt to capture certain system characteristics for a specific use of that model. Applications of a model in the field of process design include process analysis, economic, technical, and environmental evaluation, investigation of the viability of innovative designs, impacts of process parameter changes on performance, and optimization employing structural and parametric adjustments [39, 40]. Table 4 contrasts the empirical data of a packed bed reactor, whose properties served as the foundation for the simulation, with the cyclohexane conversion in the modeled conventional reactor at multiple process temperatures [41]. These qualities are shown in Table 1 previously.

Table 4. Model validation of the conventional cyclohexane dehydrogenation reactor

Temperature (K)	Cyclohexane Dehydrogenation		Relative Errors (%)
	Cyclohexane Conversion (Experimental data)	Cyclohexane Conversion (Simulation results)	
423	0.0714	0.0735	2.94
448	0.1434	0.1476	2.93
473	0.301	0.3052	1.40
498	0.5893	0.5973	1.36
523	0.8812	0.7106	1.28
544	0.8812	0.8925	1.28

Results and Discussion

Using temperature and conversion diagrams, production rates, and the suggested thermally coupled reactor, the suggested reactor's performance is contrasted with that of the traditional uncoupled reactors in this section. The aforementioned diagrams are achieved by solving the energy balance and mass equations by employing Matlab software. Hence, the advantages of the proposed thermally coupled process can be easily seen compared to the traditional uncoupled procedure that operates under the same operational situations as the thermally coupled process.

Fig. 3 demonstrates the temperature variation for nitrobenzene hydrogenation in the inner tube of the recommended reactor in the uncoupled reactor. The proposed reactor operates at a lower mean temperature than the ordinary reactor due to heat donation to the endothermic sides. As it is evident, the temperature has risen on a mild slope at the entrance of the thermally coupled reactor, meaning that the produced heat in the inner tube is greater than the heat donated to the endothermic sides. It is also noticeable that in the ordinary reactor, the temperature increases with a steep slope initially due to the high reaction rate. Afterward, a rapid decrease occurs when the output of the first bed enters the condenser.

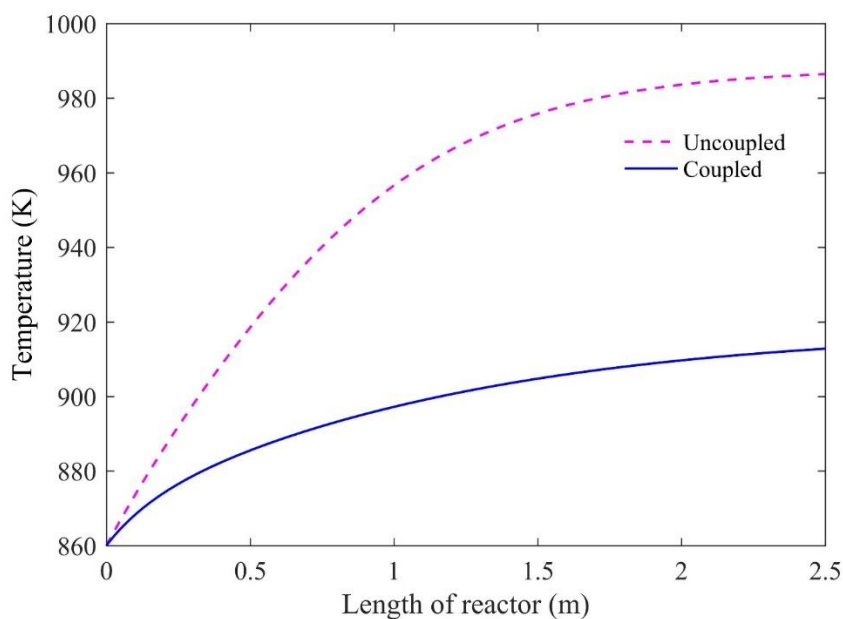


Fig. 3. Temperature profiles of the nitrobenzene hydrogenation in the coupled and uncoupled reactors

The temperature profiles in the outer tube of the recommended reactor and the uncoupled reactor for cyclohexane dehydrogenation are presented in Fig. 4 with the same conditions and characteristics as the coupled reactor. As illustrated, the temperature is constantly decreasing in the uncoupled reactor due to the endothermic nature of the reaction. In addition, a slight decline can be seen in the slope of the diagram due to lowering feed concentration, reaction temperature, and the reaction rate along the reactor. Furthermore, it is understood from the coupled reactor's profile that the received heat from the exothermic part is less than the utilized heat by the reaction at the starting point of the reactor. The temperature drops as a result, eventually reaching 502 K. Ultimately, the raised temperature differential between the exothermic and endothermic components and the accelerated pace of the endothermic process causes the temperature to rise.

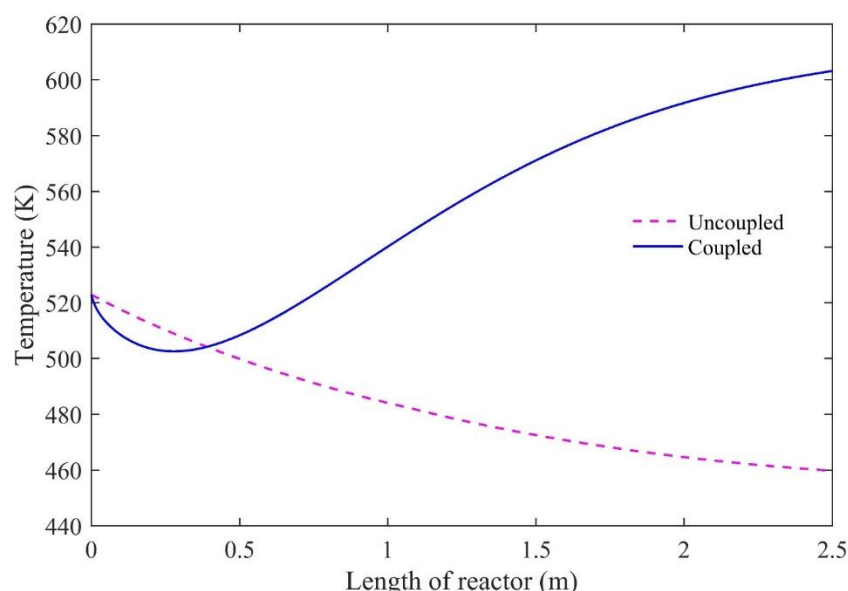


Fig. 4. Temperature profiles of the cyclohexane dehydrogenation in the coupled and uncoupled reactors

Fig. 5 demonstrates the variation of nitrobenzene conversion along the reactor for the uncoupled and coupled configurations. At the beginning of the reactors, nitrobenzene conversion increases with a steep slope caused by high reactant concentration and high reaction temperature. Then, the slope of the conversions declines. It should also be mentioned that nitrobenzene conversion in the coupled reactor is decreased from 0.65 to 0.51 compared to the ordinary reactor, respectively; it is the result of the higher mean temperature in the ordinary reactor resulting in a higher reaction rate and consequently higher conversion. Thus, the uncoupled reactor reaches more nitrobenzene conversion than the thermally coupled reactor.

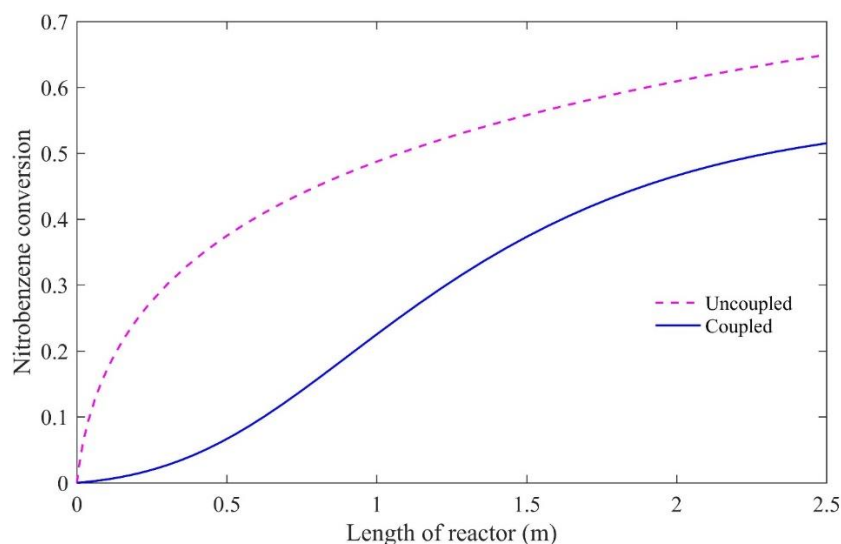


Fig. 5. Nitrobenzene conversion along with the coupled and uncoupled reactors

Fig. 6 demonstrates cyclohexane conversion in the reactors. At the beginning of the reactors, cyclohexane conversion increases with a steep slope caused by high reactant concentration and high reaction temperature. Then, the slope of the conversions declines. As can be observed, the coupled reactor's coupled conversion has improved from 0.89 to 0.97 versus the conventional reactor due to the coupled reactor's greater average temperature. In comparison to an uncoupled reactor, the thermally coupled reactor is able to convert more cyclohexane.

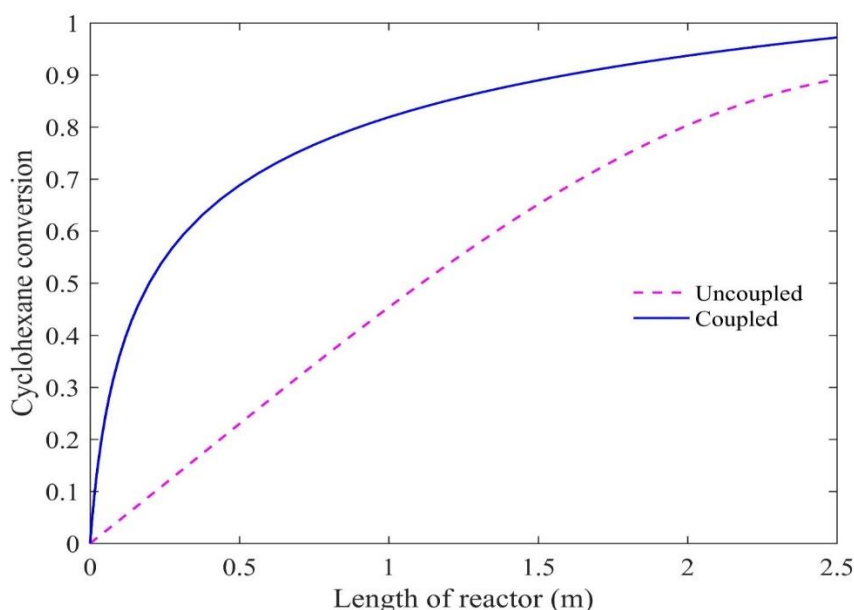


Fig. 6. Cyclohexane conversion along with the coupled and uncoupled reactors

Conclusion

In this work, a novel method was introduced for two simultaneous reactions in a multiple-tubular thermally coupled reactor. The heat essential for the endothermic process in the outer tube was generated by the exothermic reaction present in the inner tube. The cyclohexane dehydrogenation reaction was performed as an exothermic reaction in the inner tube in accordance with the suggested procedure design. The hydrogenation of nitrobenzene, in contrast, took place as an endothermic reaction in the outer tube. Thus, in addition to preventing energy waste and simultaneous production of aniline and benzene as two valuable products, the endothermic reaction in the suggested thermally coupled reactor provided the needed hydrogen for the aniline synthesis procedure. Moreover, compared to the conventional uncoupled plants, the production rate of cyclohexane was raised, while aniline production slightly declined.

Nomenclature

A_c^{Exo}	Cross-sectional area of the exothermic side (m^2)
A_c^{Endo}	Cross-sectional area of the endothermic sides (m^2)
A_i	Inside area of the inner tube (m^2)
A_o	Outside area of the inner tube (m^2)
$C_{p_i}^0$	Heat capacity of component i ($J\ kmol^{-1}\ K^{-1}$)
$C_{p_{mix}}^{Endo}$	Specific heat of gas mixture in the endothermic sides ($kJ\ kmol^{-1}\ K^{-1}$)
$C_{p_{mix}}^{Exo}$	Specific heat of gas mixture in the exothermic side ($kJ\ kmol^{-1}\ K^{-1}$)
d_p	Particle diameter (m)
D_o	Inner tube outside diameter (m)
D_i	Inner tube inside diameter (m)
F_i	Molar flow rate of component i ($kmol\ h^{-1}$)
h	Heat transfer coefficient between the fluid phase and the reactor wall ($W\ m^{-2}\ K^{-1}$)

ΔH^{Exo}	Heat of reaction in the exothermic side (kJ kmol^{-1})
ΔH^{Endo}	Heat of reaction in the endothermic sides (kJ kmol^{-1})
K_w	Thermal conductivity of the reactor wall ($\text{W m}^{-1} \text{K}^{-1}$)
K_f	Fluid thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
k	Dehydrogenation reaction's rate constant ($\text{mol m}^{-3} \text{Pa}^{-1} \text{s}^{-1}$)
K_B	Adsorption equilibrium constant for benzene (Pa^{-1})
K_P	Dehydrogenation reaction's equilibrium constant (Pa^3)
L	Reactor length (m)
m^{Exo}	Mass flow rate of the feed in the exothermic side (kg h^{-1})
m^{Endo}	Mass flow rate of the feeds in the endothermic side (kg h^{-1})
M^{Exo}	Mean molecular weight in the flow in the exothermic side (kg kmol^{-1})
M^{Endo}	Mean molecular weight in the flows in the endothermic side (kg kmol^{-1})
P	Total pressure (atm)
P_{H_2}, P_B, P_C	Partial pressures of hydrogen, benzene, and cyclohexane (Pa)
R	Reaction rate ($\text{kmol m}^{-3} \text{h}^{-1}$)
R_g	Gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
r_i	Inner tube radius (m)
r_c	Reaction rate of cyclohexane dehydrogenation ($\text{mol m}^{-3} \text{s}^{-1}$)
T^{Exo}	Temperature of the exothermic reaction side (K)
T^{Endo}	Temperature of the endothermic reaction side (K)
u	Axial velocity (m s^{-1})
u_g	Velocity of the gas phase (m s^{-1})
U	Overall heat transfer coefficient ($\text{W m}^{-2} \text{K}^{-1}$)
Z	Axial reactor coordinate (m)

Superscript

Exo, Endo Exothermic and endothermic reaction sides

Subscript

i Numerator for component

Greek letters

μ Fluid viscosity (Pa s)
 ρ Density (kg m^{-3})
 φ_s Sphericity
 η Effectiveness factor
 ν_i Stoichiometric coefficient of component i

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