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Production of Isooctane from Isobutene: Energy Integration and Carbon Dioxide Abatement via Catalytic Distillation

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ABSTRACT: Isooctane is a valuable octane enhancer for gasoline and the primary component of aviation gasoline, also known as Avgas, because of its high antiknock quality. Conventional industrial processes for isooctane production involve the steps of dimerization of isobutene, dimer separation, and hydrogenation. The efficacy of catalytic distillation (CD) and its merits, in terms of energy savings and reduction of greenhouse gas emissions, for the production of isooctane are quantitatively presented. The feed considered for the isooctane production is composed of isobutene (C_4) and inerts (isopentane) produced in refineries as byproducts of steam cracking of naphtha and light gas oil. Process flow sheets for the two routes for the production of isooctane, with and without CD, are modeled. The conventional industrial flow sheet composed of a dimerization reactor, distillation column, and a hydrogenation reactor (configuration A), is simulated using Aspen Plus. The intensified process flow sheet comprising a CD column for the dimerization, hydrogenation, and separation (configuration B) is modeled using gPROMS. A validated, nonequilibrium, three-phase model is developed in a gPROMS environment and is used to quantify the energy savings and reduction of carbon dioxide emissions achieved using a CD column for the intensified process. Results demonstrate CD to be a promising candidate to replicate the conversions and product purity obtained in the conventional process while resulting in significant energy savings, more efficient utilization of isobutene feed, and reduced carbon dioxide emissions.

1. INTRODUCTION

Recent refinery technologies have been directed at producing high-octane gasoline-blending components that are essential to increase the compliance of motor gasolines with the quality specifications and projected quantity demand.[1,2] The phase out of methyl-*tert*-butyl ethanol (MTBE) in North America, increased demand for middle distillates (kerosene and diesel) in comparison to gasoline fractions, implementation of the latest European fuel specifications, and adoption of cleaner and more stringent fuel quality specifications worldwide have necessitated efforts toward the production of greater quantities of high-octane blending components for gasoline that do not contain aromatics, benzene, olefins, and sulfur.[2-4]

In regard to these recent oil refining developments, isooctane has emerged as one of the leading gasoline additives on account of its high octane number, low vapor pressure, and zero content of aromatics and sulfur.[5-7] Isooctane is also the primary component of aviation gasoline (Avgas) because of its knock resistance and high compression ratio.[8,9] Isooctane production technology offers the scope of utilizing surplus isobutene in refineries due to the MTBE phase-out and increased refinery revenues as conversion of light olefins into gasoline blends results in increased gasoline sales. Isooctane use and production are expected to rise significantly in the near future.

The conventional process for isooctane manufacturing involves dimerization of isobutene in a fixed bed reactor with a supported acid catalyst, followed by hydrogenation in a continuous stirred tank reactor with hydrogenation cata-lysts.[7,10,11] There are various isooctane processes available commercially, varying in terms of reaction conditions, reactant conversion, and catalyst type, namely, CDIsoether, InAlk, Selectopol, SP-Isoether, NExOCTANE, etc.[7,12,13] Most conventional processes for isooctane production operate at low conversions (20–60%, with conversions differing according to

the catalyst and reactor design) to prevent catalyst sintering due to the highly exothermic reaction and to avoid the formation of higher oligomers that may result from the increased concentration of dimer in the reactor.[14-16] Conversions higher than 60% per pass are often not feasible and rare in industry because of these constraints. Our objective is to quantify the merits of catalytic distillation (CD) over the conventional reactor followed by separation process. We model the conventional process at different conversions to get an accurate comparison of results between a conventional and CD process. The detailed process flowsheet diagram for the conventional process is shown in Figure 1.

Process intensification is a principle of green engineering whereby two or more unit operations are combined into a single unit operation with the beneficial result of increased efficiency, reduced operating and capital costs, and a reduction of waste and recycle streams. The sensitivity of the isooctane process performance to various parameters such as type of catalyst, process conditions, and reactor configuration opens intriguing options for process design and intensification. CD is a green engineering technology that combines the function-alities of a chemical reactor into a distillation column by immobilizing solid catalyst particles within discrete reactive sections.[17] This distinctive feature of CD to simultaneously carry out the chemical reaction and the product separation and purification within a single-stage operation results in significant capital savings due to process intensification. The continuous removal of product from the reactive section via the distillation
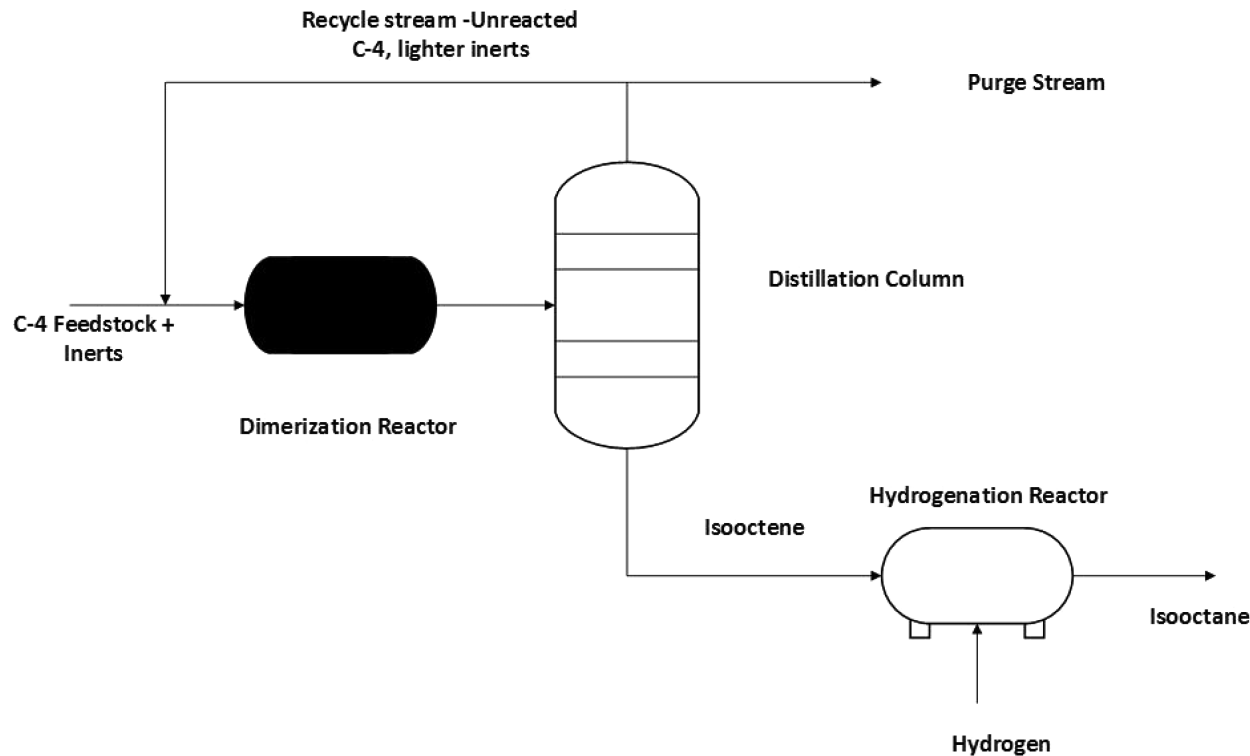
A

Figure 1. Simplified process flow sheet diagram for the conventional isoctane process.

79 action can also lead to higher conversion and selectivity,
80 particularly for reactions that are equilibrium-limited because
81 the products formed are immediately removed by distillation,
82 thereby preventing the products from participating in other
83 undesired side reactions. Other potential advantages of CD
84 include the mitigation of catalyst hot spots, improved
85 temperature control, and enhanced energy integration due to
86 conduction of an exothermic chemical reaction in a boiling
87 medium with in situ separation via distillation.

88   CD finds applications primarily for reactions in which the
89 difference in volatilities of the reactants and the products is
90 sufficiently high so that they may be feasibly separated by
91 distillation. In addition, the reaction should be exothermic and
92 should take place in the liquid phase. The isoctane production
93 process is an ideal candidate for CD operation and fits the
94 design criteria perfectly. The dimer products differ substantially
95 in volatility, which makes separation by distillation favorable
96 (see physical properties listed in Table 1). Moreover, the
97 exothermicity of both the dimerization and hydrogenation
98 reactions involved in the synthesis of isoctane from isobutene
99 reported in the literature[5,11] greatly favors a CD operation as it
100 would fulfill most of its energy requirements for product
101 separation from the exothermicity of the reactions. This would
102 lower the heat duty of the reboiler. An added advantage of in

103 situ separation of products in CD utilizing the reaction heat is
104 the reduction of the formation of higher oligomers of isobutene
105 such as dodecene (side reactions), thus resulting in higher
106 product selectivity. CD is, therefore, a very promising option
107 for isoctane production. The objective of this research is to
108 quantify some of the above merits.

109   The effectiveness of a CD process compared to conventional
110 non-CD processes has been studied for various reactions by
111 many researchers.[18−20] The intensified process using CD
112 results in higher conversion as well as reduced total condenser
113 and reboiler duties. However, to the knowledge of the authors,
114 in the literature to date, no systematic, quantified work has
115 been done toward assessing the savings of energy and reduction
116 of greenhouse gases when a reactor and distillation column are
117 replaced with a CD column for the process of isoctane
118 production from isobutene. This is an industrial reaction of
119 great significance to downstream refinery operations because
120 butene isomers are obtained as byproducts of the steam
121 cracking of naptha and light gas oil. To achieve a detailed
122 comparison and quantification of the merits of CD, we have
123 modeled both the conventional isoctane production process
124 (reactor and distillation) and the intensified CD process. The
125 conventional isoctane process is modeled in Aspen Plus, one
126 of the most extensively used chemical engineering packages.
127 The intensified CD process is modeled using gPROMS, an
128 equation-oriented advanced modeling and simulation tool.
129 Though results from process simulations and actual process
130 operations differ to some extent, simulation software tools
131 generally provide quite reliable and accurate information on
132 process operations and the influence of process parameters
133 because of their comprehensive thermodynamic packages, rich
134 component data, and astute calculation techniques. Hence, the
135 modeling results could provide comparison between perform-
136 ance of competing technologies in real operations.

Table 1. Boiling Point and Density of Isobutene and Its Dimer Product Isoctane

	isobutene	isoctene (dimer)
molecular weight (g/mol)	56.107	114.23
boiling point (°C)	−7.2 °C (1.013 bar)	99 °C
density (g/cm³)	0.626 (at boiling point, 1.013 bar)	0.69

The process configurations for the conventional process and the catalytic distillation process have been modeled in different software systems (Aspen Plus and gPROMS) on account of modeling constrainsts. The CD pilot plant runs were modeled using a validated, three-phase, rate-based nonequillibrim model coded in gPROMS. The current gPROMS library does not have reactor models that can handle components in both the liquid and vapor phase. Current reactor models in gPROMS can handle only gas-phase reactions. The gPROMS library is also presently devoid of distillation column models that quantify reactor and condenser duties for a given product purity. The authors also note that the model equations for the reactor and distillation models remain the same in different software libraries. The differences in software results arise from thermodynamic packages for calculation of physical properties, component data, and calculation techniques (solvers). These differences would not influence the results appreciably.
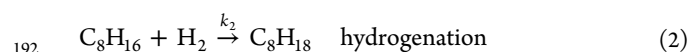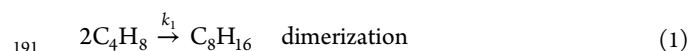
There are previous literature reports on quantification of energy savings obtained in a CD process against the conventional processes for other reaction systems.[18,21−23] Reference 18 reports a reduction of 20−40% in utility requirements for the synthesis of methyl *tert*-butyl-ether when the conventional process configurations were replaced by CD configurations. Energy requirements were also stated to get reduced by 25% on switching to CD technologies in real MTBE production units in ref 22. For the synthesis of dimethyl ether, CD has been reported to bring about 20% reduction in annual utility costs.[21] While refs 18, 21, and 23 report comparisons based on Aspen Plus simulations, ref 22 reports energy savings brought about by CD in real refinery unit operations. It is anticipated that energy savings should be much higher when highly exothermic reaction systems such as oligomerization and hydrogenation reactions are carried out in a CD configuration. This is indeed the result we obtained in this study.

In this study, results from both process configurations (conventional process versus CD) are compared at the same product purity (0.36 mole fraction of isooctane) on the basis of per kilogram of product.[24,25] A comparison of the utility requirements and isobutene feedstock utilization is also performed. The savings in energy requirements and the elimination of isobutene waste are then quantified to relate the effectiveness of CD as compared to the conventional process.

This study uses a validated, flexible, three-phase, nonequilibrium model coded in gPROMS using overall mass-transfer coefficients for depicting the CD column performance (discussed in section 3.2). This research is hence able to compare the energy consumption and profiles of temperature and composition of the isooctane process with and without the use of a CD column.

2. REACTION: ISOBUTENE TO ISOOCTANE

The reaction system selected for isooctane production is the dimerization of isobutene to isooctene with subsequent hydrogenation to isooctane (illustrated in eqs 1 and 2).

$$2C_4H_8 \xrightarrow{k_1} C_8H_{16} \quad \text{dimerization} \tag{1}$$

$$C_8H_{16} + H_2 \xrightarrow{k_2} C_8H_{18} \quad \text{hydrogenation} \tag{2}$$

These reactions are of considerable industrial importance because a lower quality fuel, isobutene, is converted to a high octane number fuel, isooctane. The dimerization reaction is highly exothermic with a heat of the reaction of $\Delta H = -82.9$ kJ/mol.[5,16] A RSTOIC reactor model in Aspen Plus also gave similar results. The RSTOIC model predicted the heat of reaction to be −76.2 kJ/mol at 1 atm and 300 K for the isobutene dimerization reaction. Hydrogenation reactions of alkenes are known to be exothermic, but this was also verified (estimated around −109.55 kJ/mol) by running a RSTOIC Aspen model. The exothermicity of both reactions makes CD an ideal candidate for in situ heat utilization toward separation of products.

The reaction kinetic data for the dimerization and the hydrogenation reactions in the isooctane production process were incorporated from previous experimental studies carried out in our laboratory[25] using a nickel sulfate and a Pd catalyst separately supported on γ-Al$_2$O$_3$.[24] These kinetic data correspond to the liquid-phase oligomerization and hydrogenation of isobutene obtained in a 300 mL Parr autoclave reactor. The dependence of the reaction rate constant on the reaction temperature was based on the Arrhenius equation, $k = Ae^{-(E/RT)}$ where the reaction constants k_1 and k_2 for the dimerization and hydrogenation, respectively, are given below.

Dimerization Reation:

$$r_{C_4H_8} = \frac{d}{dt}[C_{C_4H_8}] = -2k_1 C_{C_4H_8}^{3.186} \tag{3}$$

$$k_1 = 175.1818 \exp\left(\frac{-22184}{RT}\right) \tag{4}$$

The units of C and rate of reaction, r, are mol/s and mol/s/kg-cat, respectively.

Hydrogenation Reaction:

$$r_{C_8H_{18}} = \frac{d}{dt}[C_{C_8H_{18}}] = k_2 x_{C_8H_{18}}^{0.3} P_{H_2}^{0.33} \tag{5}$$

$$k_2 = 92.4788 \exp\left(\frac{-20678}{RT}\right) \tag{6}$$

The units of P_{H_2} and rate of reaction, r, are psig and mol/s/g-cat, respectively.

3. PROCESS SIMULATION

3.1. Conventional Reactor Separation Process (Configuration A). Figure 1 shows a simplified process flow diagram for the isooctane production process in a conventional non-CD process. The feed, composed of isobutene and isopentane as an inert, is first dimerized to isooctene in the reactor. The more volatile nonreacted monomer (isobutene) is then separated from the heavier dimer product (isooctene) in the distillation column and sent back to the reactor. The isooctene then enters the hydrogenation reactor, where the hydrogenation reaction occurs and the final hydrogenated product, isooctane, is obtained.

The flowsheet diagram in Figure 1 is simulated in Aspen Plus. The main processing equipment units are a mixer, a plug-flow fixed bed reactor (PFR), a distillation column, and a stirred tank reactor (CSTR). The mixer functions to enable the recycle of the overhead unreacted monomer back into the reactor. The column functions to separate the lower molecular weight volatiles C-4 and C-5 hydrocarbons from the isooctene. The stirred tank reactor serves as the hydrogenation reactor for conversion of isooctene to isooctane.
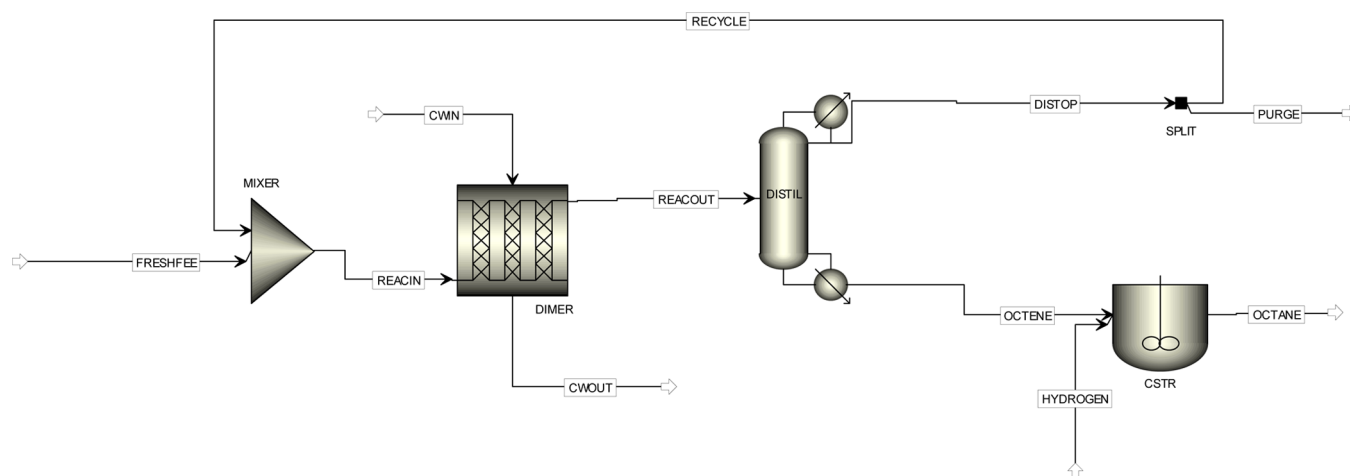
Figure 2. Simulation of the conventional reaction separation technology (configuration A) in Aspen Plus environment.

Figure 2 shows the detailed Aspen Plus simulation environment for configuration A. To model the conventional reaction separation process, the process flow diagram, stream-flow rates, and equipment specifications were based on data available in the literature for the NExOCTANE process for the production of isooctane.[13] The Aspen process model uses the kinetic model for the catalyst system discussed in section 2. The idea presented here is to compare the conventional process flowsheet and the CD process flowsheet for the isooctane process for the same catalyst system.

A constant feed with a molar rate of 1.5 kg/sec (corresponding to a feed rate of approximately 11 880 lb/h of isobutene feed similar to the feedrate of around 13 700 lb/h as stated for the NExOCTANE process[13]) is fed to the reactor in an equimolar ratio of isobutene and isopentane. Isopentane represents the inert feed component which in a real refinery comprises C-3, C-4, and C-5 alkanes. A jacketed tubular (plug-flow) reactor is used in the model. The reactor functions at 25 atm and 370−410 K (temperature varies along the length of the reactor) and produces isobutene at varying conversions (25, 50, or 90%) depending on the case investigated. Temperature and pressure for the reactors are as specified for the NExOCTANE process while the reactor design paramters (tubes and reactor length) are modified according to the isobutene conversion. Plug-flow reactors are known for achieving the highest conversion per unit volume, and they also require lower maintenance and less shutdown times.[26] Because the dimerization reaction is highly exothermic, the reactor is cooled via a countercurrent stream of cooling water.

An equilibrium-based rigorous two-phase fractionantion model (RADFRAC) was used to model a 14-tray distillation column; the output stream from the reactor was injected as feed onto the seventh tray. The adjustment for process parameters (number of distillation stages, reflux ratio, reboiler duty) was set so as to result in less than 1% iso-butene in the bottom product and less than 1% of iso-octene in the top product. The distillation column was operated in the pressure range of 10−15 atm with no pressure drop between the stages for different scenarios of conversion and recycle. The hydrogenation reactor was modeled by a two-phase continuous stirred tank reactor operating at 3 MPa and 330 K (NExOCTANE process conditions specified in ref 13) with hydrogen injected into the bottom product (isocotene) from the distillation column.

In an actual refinery operation, the recycle ratio is often varied depending on the product requirements. The actual recycle ratio for the NExOCTANE process was not available in the literature. Therefore, the simulation for configuration A was run under varying recycle ratios, and the results were recorded for comparison with the CD model (configuration B). The CD model was run at total recycle because our experimental CD data was obtained at total reflux. For the conventional process, we have simulated (configuration A) at different conversions and different recycles. All cases for configuration A were set so as to produce isooctane at around 0.36 molar fraction of the hydrogenated product (iso-octane) in the final product stream because our CD experiments produced isooctane at this purity. The CD model described in the next section also produces a 0.36 molar fraction of iso-octane in the reboiler; therefore, a comparison of the energy requirements per kilogram of product is justified. As expected, results for the conventional reaction separation process showed significantly larger cold utility requirements due to the intense cooling water requirements for cooling the dimerization and hydrogenation reactors (Table 2).

3.2. Catalytic Distillation Process (Configuration B). A 23 ft (7 m) pilot CD process unit (Figure 3) was used for obtaining the CD process data.[19,20] The CD column is composed of two reaction zones and three separation zones. Isobutene as a feed is injected just below the dimerization zone. The dimerization reaction is exothermic, and the in situ reaction heat is utilized to enhance separation of volatiles, aiding heat mitigation and temperature control of the column, thus cutting down cooling water requirements and preventing catalyst sintering. The separation of the volatiles and the products also minimizes consecutive oligomerization reactions. The less volatile and denser dimerized product, isooctene, moves downward to the hydrogenation zone, where it reacts with hydrogen to produce isooctane. The hydrogenation reaction is highly exothermic; therefore, the produced heat in the hydrogenation section further aids vaporization of volatile components and reduces the reboiler load. The nonreacted isobutene is stripped in the lower separation zone of the column, and a pure isooctane product leaves the column. The CD column in our laboratory functions at total reflux; the nonreacted isobutene, isopentane, and the trace amounts of evaporated isoctane and isooctene are essentially totally condensed in the condenser and returned to the column.

D

Table 2. Comparison of Energy Requirements, Monomer Utilization, and Carbon Dioxide Emissions with and without Catalytic Distillation

recycle	total cooling (KW/kg product)	total heating (KW/kg product)	nonreacted isobutene (kg/kg product)	CO_2 produced (kg/kg product)
Conventional Process: 25% Conversion				
0%	−5 295	5 815	0.75	0.895
25%	−6 450	7 174	0.5625	1.105
50%	−8 201	8 123	0.375	1.251
75%	−9 334	8 869	0.175	1.366
100%	−11 110	10 719	0	1.651
Conventional Process: 50% Conversion				
0%	−3 795	2 480	0.5	0.382
25%	−4 319	2 478	0.375	0.381
50%	−4 988	3 027	0.25	0.466
75%	−5 304	3 420	0.125	0.527
100%	−5 605	3 787	0	0.583
Conventional Process: 90% Conversion				
0%	−2 552	**944**	0.1	**0.145**
25%	−2 765	**1 142**	0.075	**0.176**
50%	−4 363	2 210	0.05	0.340
75%	−4 970	2 614	0.025	0.402
100%	−5 095	3 221	0	0.496
CD Process: Total Conversion				
100% recycle	**−1 520**	**1 660**	**0.00004**	**0.256**

A validated three-phase, rate-based, nonequilibrium model using overall mass-transfer coefficients is used for depicting the CD column performance. This CD model was validated using our experimental data for the production of isooctane from isobutene.[19,20] Our earlier paper[27] presented in detail the equations including mass, energy, and component balances; rate expressions; and equilibrium and summation equations for the CD model. The model used in-house developed binary mass-transfer coefficients for the packing used in the CD experiments. The model was coded in gPROMS 3.4.3, an equation-oriented software developed by Process Systems Enterprise (London, U.K.) for modeling, simulation, optimization, and experimental design studies. Because a rate-based, nonequilibrium approach[28,29] was utilized for modeling the CD process, gPROMS was preferred over Aspen Plus for the modeling of the catalytic distillation column. Accommodating rate expressions for mass transfer to the heterogeneous catalyst surface adds complexity to the rate expressions. gPROMS offers the advantage of coding rate expressions involving mass-transfer coefficients and interfacial areas directly into the interface in an exact form.

4. RESULTS AND DISCUSSION

This section compares the optimized energy and mass balance results for the conventional reactor separation process (configuration A) and the CD process (configuration B). Various process parameters are compared between the two configurations that highlight the efficiency and advantages of
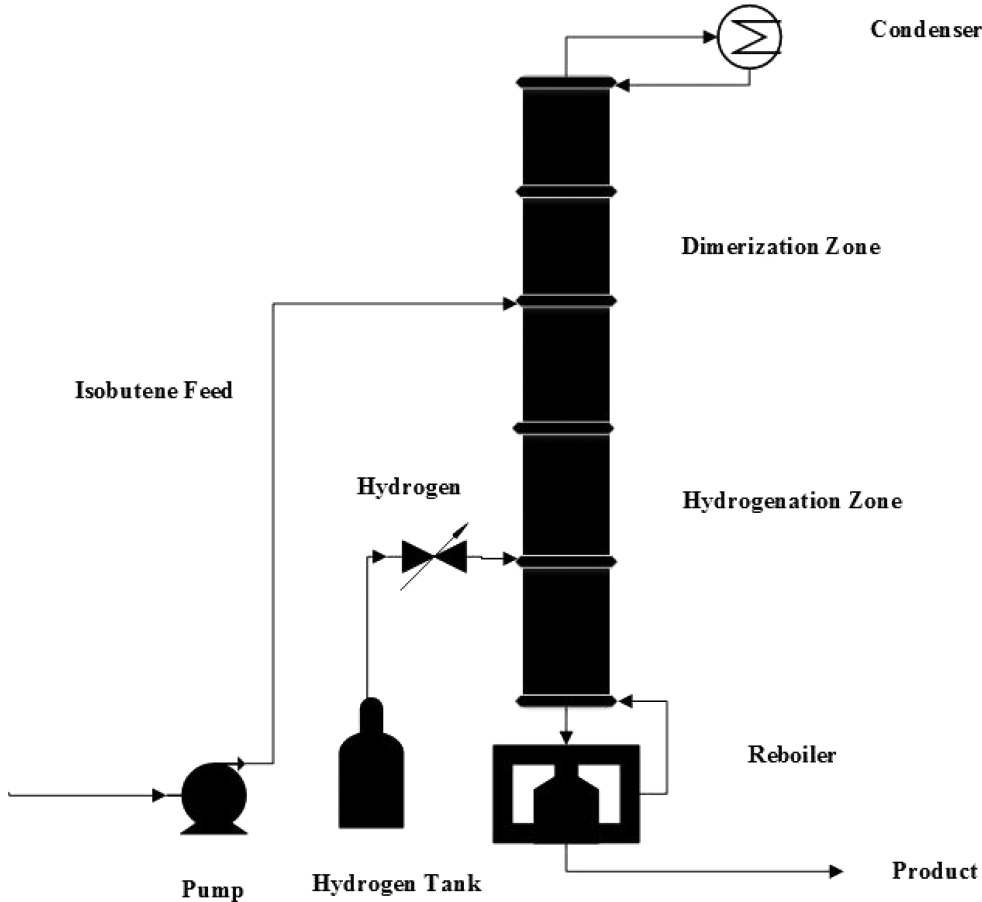
Figure 3. CD pilot plant at University of Waterloo for the production of isooctane from isobutene.
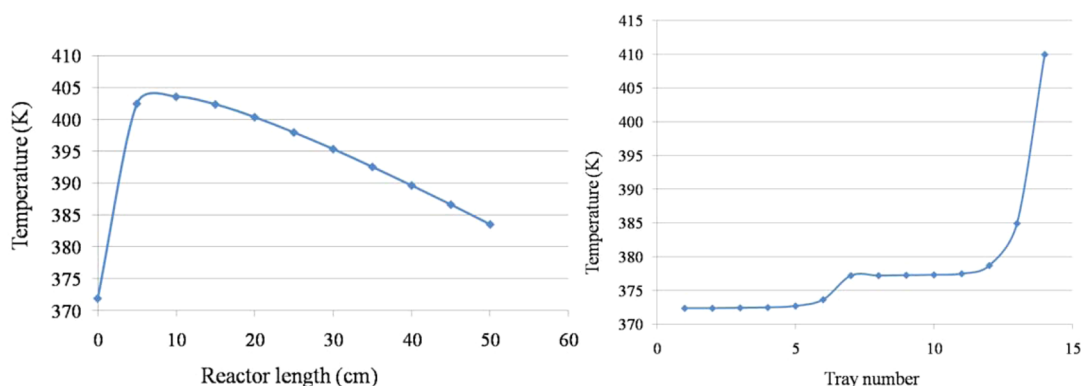
Figure 4. Profiles for reactor temperature (left panel) and distillation column (right panel) for configuration A.
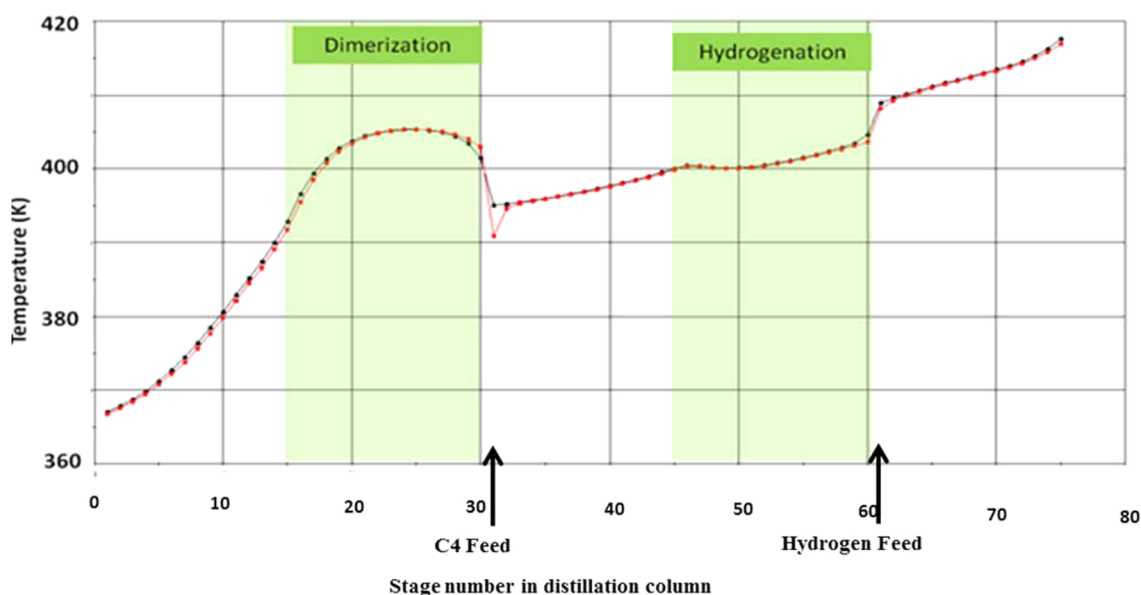

Figure 5. Profiles of temperatures along CD column (configuration B) for the production of isooctane from isobutene and H_2. Nonequilibrium three-phase gPROMS model (black, vapor phase; red, liquid phase).

the CD technology over the conventional reactor separation process.

Because energy integration provided by CD is the primary focus of investigation, the total energy consumption and optimized cooling and heating requirements of configuration A are compared with those of configuration B. Because the CD process can operate under different energy and mass balances for the same overall product conversion, the optimum parameters of the recycle ratio and vapor boil-up ratio were obtained by minimizing the energy needs of the CD column while maintaining the same octane purity and monomer separation between the two configurations. A product purity of 0.36 molar fraction of isooctane is the criterion used in the calculations of energy requirements per unit mass of isooctane produced for both configurations A and B.

4.1. Profiles of Temperature. Figure 4 depicts the temperature profile along the jacketed water-cooled dimerization reactor and the distillation column for configuration A for a 50% isobutene conversion case. Temperature profiles for processes are important indicators to study and manipulate thermal fluxes that enter and exit the system at different stages. The reactor length is 0.5 m. Because it hosts an exothermic dimerization reaction, the reactor temperature rises from 370 K

at the inlet to about 405 K at 10 cm and then drops to 383 K at the exit because of counter-current cooling via water at 300 K. The temperature profile in the distillation column varies from 370 K below the condenser to 410 K above the reboiler.

For configuration B, the gPROMS CD model assumes 75 slices with two reaction zones: a dimerization zone from slice 15 to 30 and a hydrogenation zone between slice 45 and 60. The hydrocarbon feed (a mixture of 50% isobutene and isopentane) is injected at slice number 30 while the hydrogen feed (0.25 mol H_2/mol isobutene) is injected at slice 60. The feed lines in the actual CD column were not heated; therefore, a steep temperature drop is observed at the two feed injection points. The temperature profile along the column for vapor (black) and liquid (red) are shown in Figure 5. It increases from 365 K at the condenser to 385 K below the dimerization zone. In the dimerization zone, the temperature suddenly increases to about 405 K as a result of the exothermic reaction. Then the temperature suddenly decreases because of injection of the feed (which was not heated) at slice 30, below the reaction zone. The temperature continues to rise in the hydrogenation zone because of the high exothermicity of the hydrogenation reaction and lower hydrogen feed rates. The temperature drop at the other feed injection point for
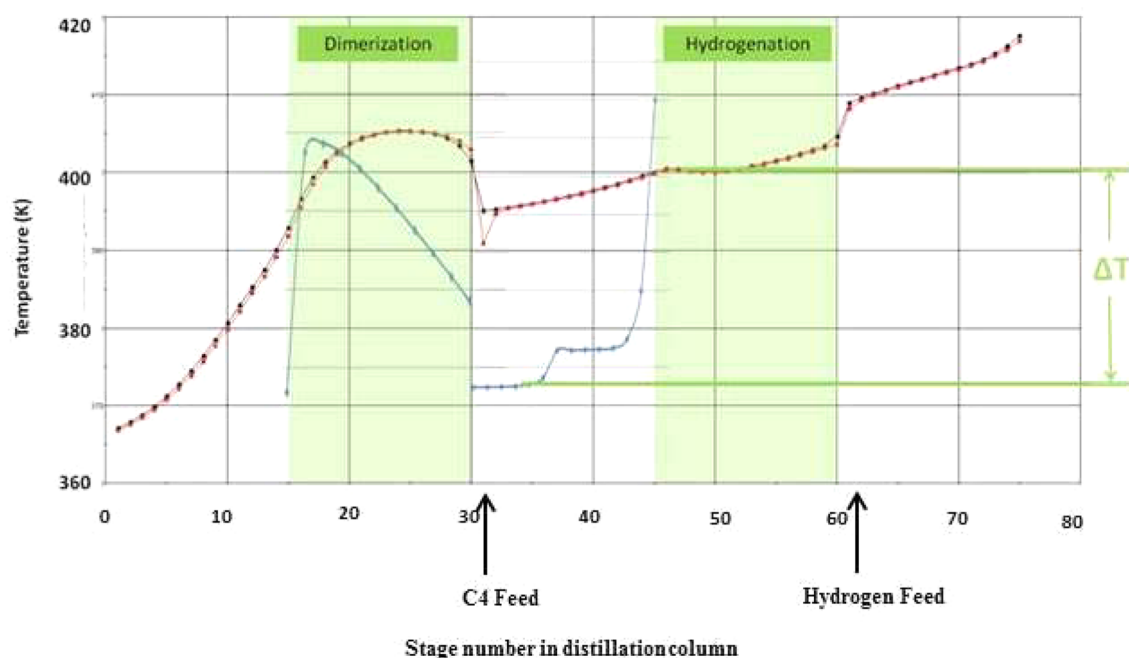
Figure 6. Comparison of the temperature profiles, configuration A (blue curve) and configuration B (red curve).
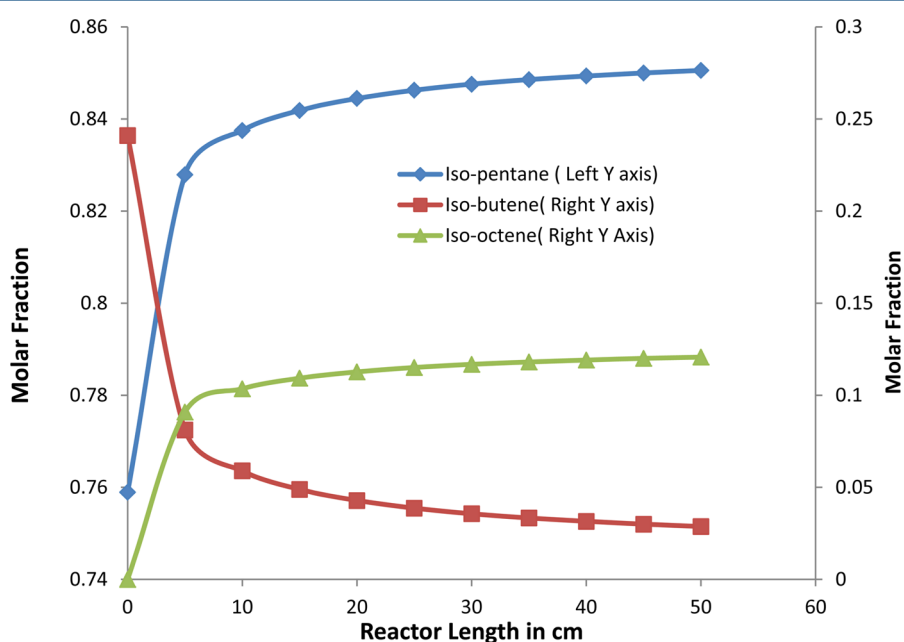

Figure 7. Profiles of liquid molar fraction along reactor simulated for configuration A (30% recycle).

hydrogen, just below the hydrogenation zone (slice 60), is not very steep. Hydrogenation of isooctene is a more exothermic and faster reaction than the oligomerization of isobutene. Second, the hydrogen feed rate in the hydrogenation section is 1/4 times that of the feed rate (isobutene and isopentane) in the oligomerization section in the CD setup. A combination of a higher, faster heat generation and lower feed rate decreases the steep temperature drop at the hydrogen injection point.

In Figure 6, the temperature profiles with and without CD are superimposed over each other to effectively provide a comparison. The blue curve depicts the temperature profile in the conventional reactor separation process (configuration A) whereas the red curve depicts the temperature profile in the CD

process (configuration B). The blue curve is discontinuous because the process equipment (reactor and distillation column) are at different temperatures. A significant amount of energy is wasted in cooling the reaction products, and then heat is required again to bring them to the separation column temperature to aid in the separation. This is an area that significantly shows the benefits brought to the process by employing CD. The CD process can be assumed to be an adiabatic reactor because both the reaction and separation units are housed in one piece of equipment and all of the reaction heat generated in situ is utilized to aid in the product separation. This provides substantial savings in the energy for a CD process, which will be discussed in section 4.3.
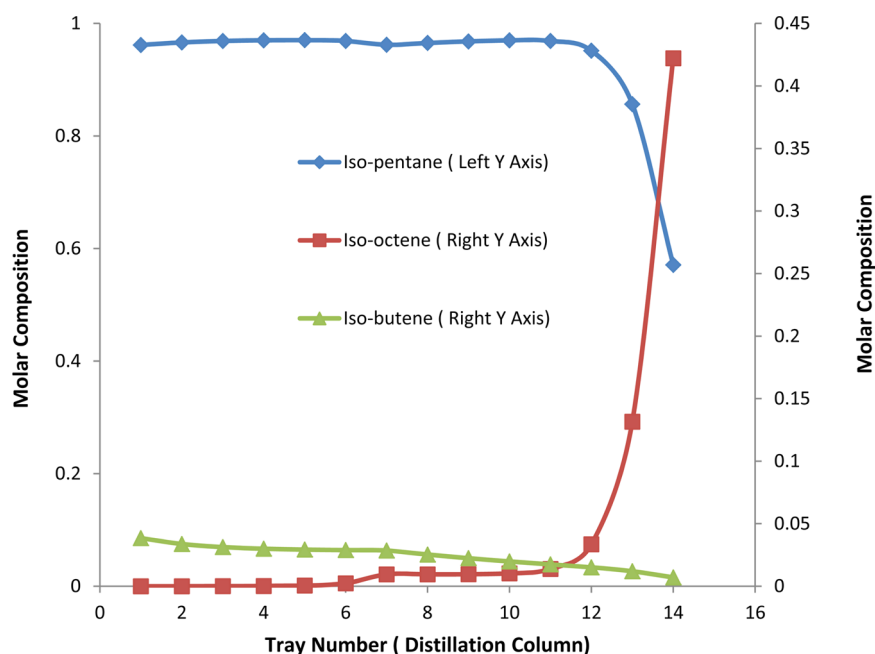
Figure 8. Profiles of liquid molar fraction along distillation column simulated for configuration A.
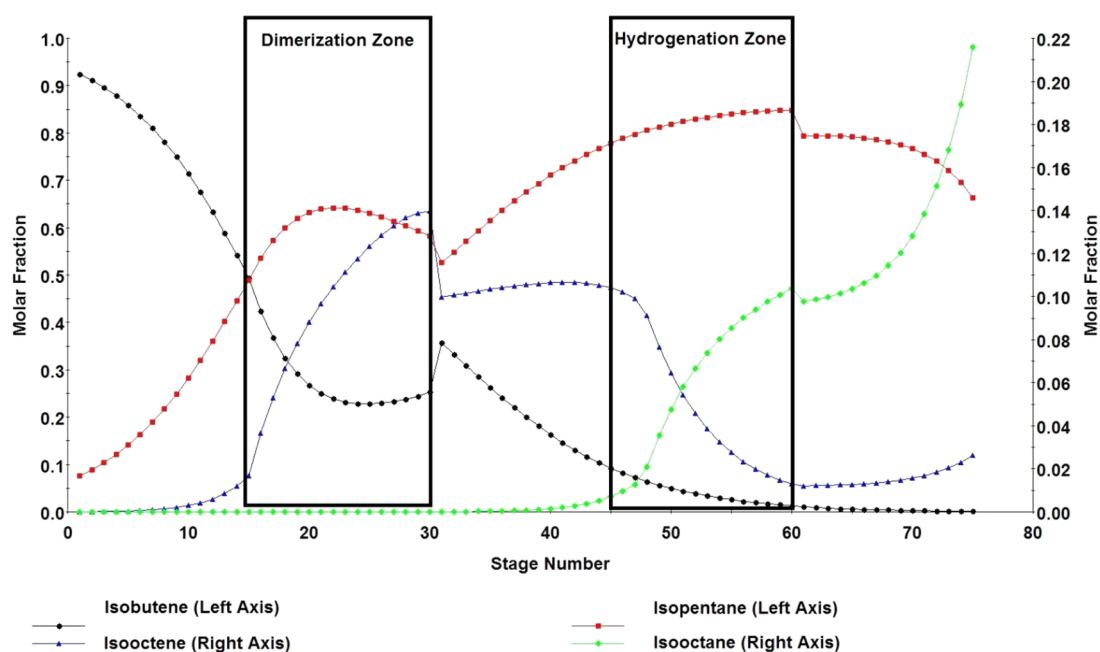

Figure 9. Liquid molar fraction profiles along CD Column (configuration B).

4.2. Profiles of Concentration. The simulated mole fraction profiles along the reactor and the distillation column (right) are shown in Figures 7 and 8. In the concentration profile along the reactor length (Figure 7) for a recycle ratio of 30%, the isobutene is consumed and its molar fraction decreases from 0.25 to 0.03 while isooctene is produced and its molar fraction increases from 0 to 0.12.

Figure 8 shows the composition profiles with respect to stages along the distillation column in configuration A where because of the product separation, the isooctene concentration rises up to 0.43 molar fraction at the last stage. Concentrations of the volatiles isobutene and isopentane show a decreasing trend. They have higher concentrations in the upper stages.

Figure 9 shows the composition profiles along the CD column with respect to stage number for configuration B. The mole fraction of the reacting monomer, isobutene, continuously drops from the top to the bottom. There is a sharp peak in mole fraction around stage 30 due to the feed injection (feed line was not heated) at this stage. Below the condenser the concentration decreases because of physical separation while in the dimerization zone, because of the simultaneous reaction and separation, the slope of the curve is much higher. The mole fraction of the dimerization product, isooctene, first increases in the dimerization zone and then decreases in the hydrogenation zone. The mole fraction of the final product, isooctane, is zero in the zones above the hydrogenation because it is the least volatile component. Isooctane starts to increase in the
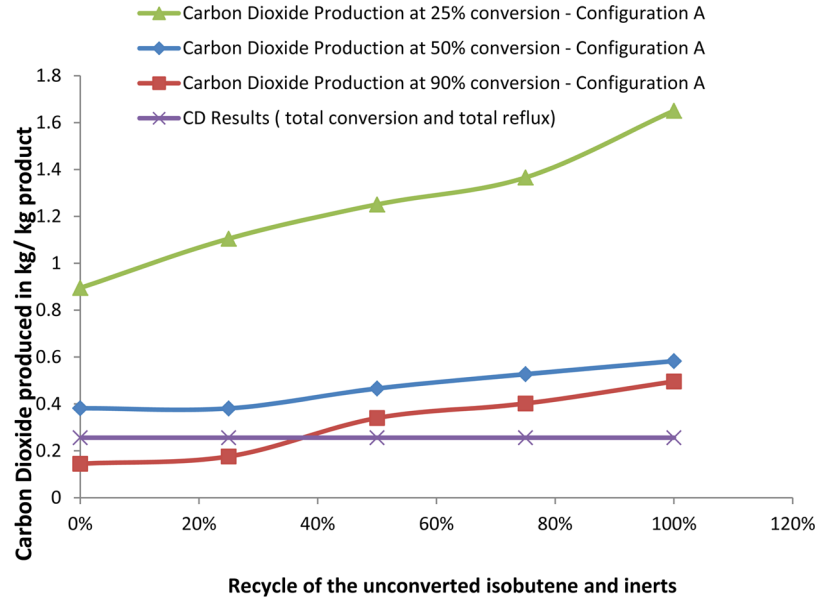
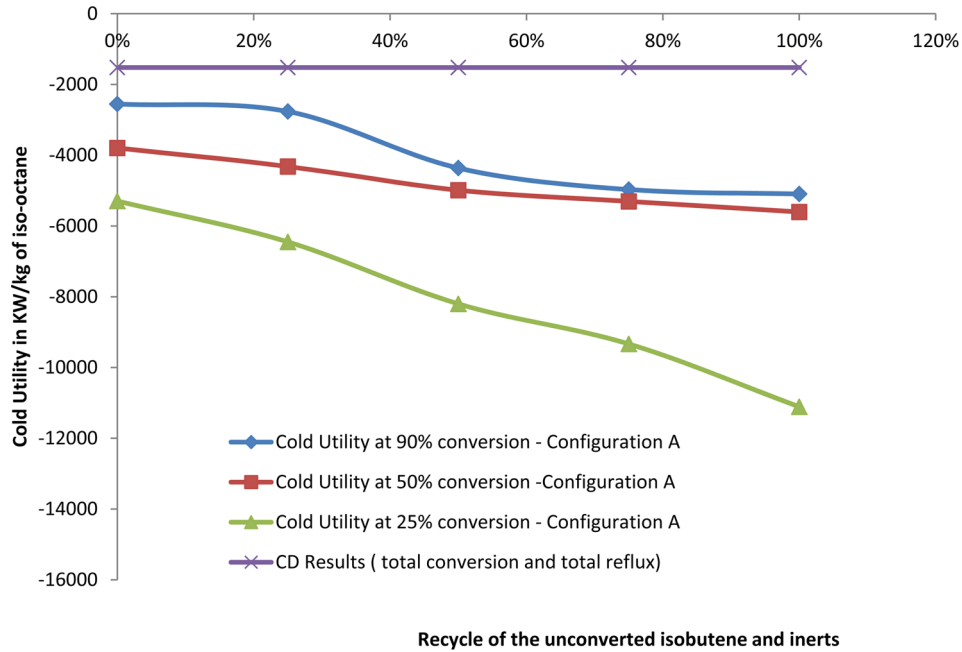**Figure 10.** Heat duty as a function of recycle, CD versus configuration A.

Figure 11. Cold utility requirements as a function of recycle, CD versus configuration A.

Table 3. Pounds of CO_2 Produced by Steam−Electric Generators for Different Fuels[30]

fuel	lbs of CO_2 per million Btu	heat rate (Btu per kWh)	lbs CO_2 per kWh
coal (bituminous)	205	10 107	2.08
coal (sub-bituminous)	212	10 107	2.16
coal (lignite)	215	10 107	2.18
natural gas	117.080	10 416	1.22
distillate oil	161.386	10 416	1.68
residual oil	173.906	10 416	1.81

hydrogenation zone and reaches about 18% above the reboiler. Reboiler heat increases the composition of isooctane to 0.36 molar fraction in the final product. Isopentane is the inert

component. Under the column operating conditions of 140 psi, it boils at 403 K. This temperature is breached only in the lower sections of the column, and as evidenced by the concentration profile in Figure 9, there is a buildup of isopentane in the lower sections of the column. In the upper sections of the column, isopentane exists mostly as a liquid and in trace amounts in vapor. Isopentane comes out with the reboiler product where its concentration is almost the same as in the feed and is removed together with the product stream, completing the mass balance. The composition of the final product in the reboiler is 0.361 molar fraction isooctane, 0.493 molar fraction isopentane, 0.045 molar fraction isooctene, and less than 0.01 molar fraction isobutene.

4.3. Energy Consumption. Energy efficiency for chemical processes is an area of high interest in an era of rising energy
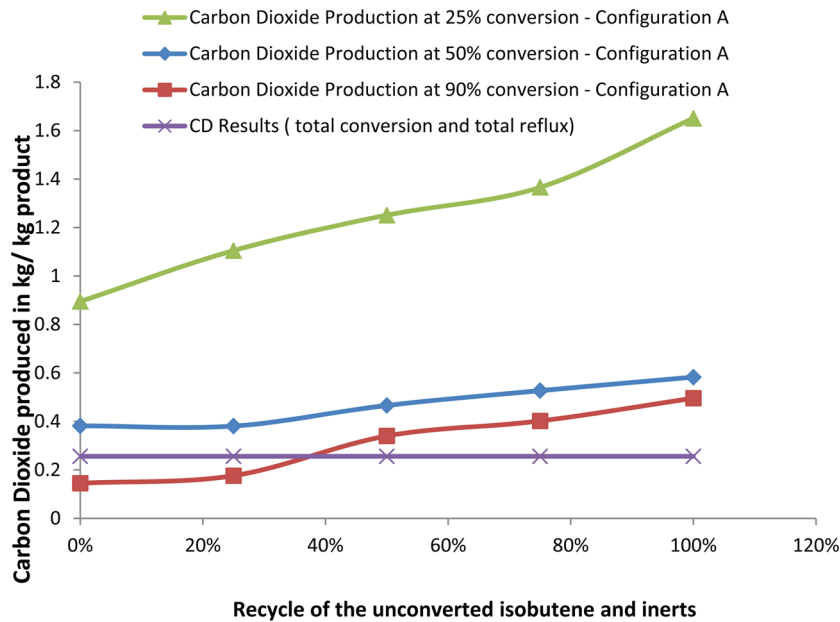
Figure 12. Carbon dioxide produced in the process as a function of recycle, CD versus configuration A.

Table 4. Effect of Addition of Hydrogenation Reaction on the Energy and Mass Balance of CD Column

CD model	feed (mol/s)	reboiler duty (W)	condenser load (W)
dimerization only	isooctene: 0.000 25	14.95	13.04
	isopentane: 0.000 27		
dimerization plus hydrogenation	isooctene: 0.000 25	13.3	12.1
	isopentane: 0.000 27		
	hydrogen: 0.000 063		

478 costs and environmental concerns. The most noteworthy
479 benefit that CD brings to the isooctane production process is in
480 terms of significant reductions in utility requirements. Table 2
481 lists the total energy consumption per kilogram of isooctane
482 produced with and without CD at different recycle rates and
483 different conversions. Comparisons are made per unit mass of
484 product (per kilogram of isooctane) at the same purity (0.36
485 molar fraction iso-octane), so varying flow rates between the
486 two configurations ceases to be a factor. The conventional
487 process (configuration A) is modeled at varying conversions
488 and reflux ratios, whereas the CD process (configuration B) is
489 modeled at total reflux. Results demonstrate that at all
490 conversions and recycle rates, the CD process requires
491 significantly less cold utilities (up to 7 times savings in cold
492 utilities). This is expected because there is massive cooling
493 water consumption in a conventional reactor separation process
494 to cool the reactor and to protect the catalyst from deactivation
495 and products from the exothermic reaction heat before they
496 enter the separation units. In a CD process, the in situ heat
497 generated from the exothermic reactions is dissipated from the
498 reaction zones toward separation of products so that minimal
499 cooling energy is required. In the case of hot utility
500 requirements, CD outperforms configuration A at all
501 conversion and recycle scenarios except at very high isobutene
502 conversions of 90% and low recycle rates. It should be noted a
503 90% conversion of isobutene is not feasible in an industrial
504 reactor configuration and that conversions in isobutene
505 dimerization processes are typically kept low, in the range of

506 20−60%, to increase the lifetime of the catalyst and enhance
507 selectivity of dimer by reducing the formation of the
508 byproducts, i.e., trimers and higher oligomers. Our simulation
509 results demonstrate CD can provide significant reduction of hot
510 and cold utilities for the isobutene dimerization process.
511 Moreover, Table 2 also depicts that CD leads to significantly
512 better utilization of the monomer isobutene, as an added
513 benefit for the isooctane process. Figures 10 and 11 relate the
514 significant energy integration CD brings into the isooctane
515 production process via reduction in utility requirements.

516 **4.4. Reduction in Carbon Dioxide Emissions.** While the
517 focus of this research is on energy savings provide by CD, this
518 study also provides quantitative estimates translating energy
519 savings into reduction of carbon dioxide (CO_2) and GHG
520 (greenhouse gas) emissions. Reduction of CO_2 and GHG
521 emissions for a process provides both economic and environ-
522 mental merits. As an economic factor, reduction in CO_2 and
523 GHG emissions changes the evaluation of energy efficiency
524 improvements (as determined by environmental regulations
525 and market economy) and also provides viability and
526 sustainability for projects that otherwise would not be
527 economical.

528 Table 2 compares the energy requirements in CD
529 configuration (kilowatt per kilogram of isooctane product)
530 for the isooctane process against various process parameters for
531 configuration A. Results demonstrate significant cooling water
532 savings (up to 7 times) at varying recycle ratios and significant
533 cooling and hot water duties at higher recycle ratios (up to 11
534 times) in the CD configuration. The challenge is to relate these
535 energy savings into GHG savings by finding a suitable
536 conversion ratio. Figures for CO_2 reductions are achieved via
537 emission factors provided by the U.S. Energy Information
538 Administration (EIA),[30] that compute the amount of CO_2
539 produced per kilowatt hour (kWh) for specific fuels and specific
540 types of generators. These indicators are listed in Table 3.

541 Most distillation columns in refinery operations have water-
542 cooled condensers using cooling water that is inexpensive.[31]
543 Cooling operations in the condenser is normally achieved via
544 large volumes of water. This practice essentially does not

contribute to CO_2 emissions. Hence, only the hot utilities were scaled by the conversion factor in calculating the CO_2 emissions. Natural gas is the preferred fuel for use in petroleum refineries utility systems;[32,33] hence, the conversion ratio for natural gas (1.22) was used.[30] Because we are directly scaling the hot utility requirements by an emission factor, the relative savings in carbon dioxide emissions is the same as the hot utility requirements (higher savings in carbon dioxide emissions at higher recycle ratios (up to 11 times)). Results for carbon dioxide emissions in terms of kilograms per kilogram of isooctane are tabulated in the last column of Table 2 and also shown in Figure 12.

As discussed earlier, most conventional reactor separation configurations run at conversions between 20% and 60% per pass. Assuming a conventional process operating at 50% conversion and 100% recycle, a reduction of 0.327 kg of carbon dioxide emissions is achieved per kilogram of isooctane product. Considering an annual production of 520,000 tons of isooctane product from a NExOCTANE process,[34] this translates to a reduction of 170,000 tons of carbon dioxide emissions per year.

4.5. Effect of Reaction Heat on the Reboiler and Condenser Loads. Results in section 4.3 demonstrated a significant reduction in reboiler duty in the CD operation for an exothermic process. To further explore the effect of the hydrogenation reaction heat on the energy balance in the CD process, two CD models were compared: a CD process with dimerization only and a CD model with two reactions, namely, dimerization and hydrogenation. When the hydrogenation reaction was carried out in the same CD column for dimerization, a 20% decrease in the reboiler and condenser duties was observed, as listed in Table 4. These results are expected because of the exothermicity of the hydrogenation reaction.

5. CONCLUSION

The efficiency of a green reactor engineering technology, CD, in terms of energy integration and material savings is compared to a conventional reactor and distillation process for the industrial production of isooctane from isobutene. Results establish the efficiency of the CD technology over the conventional reactor separation technology in terms of energy requirements and isobutene feed utilization. The CD model predicts significant cold and hot utility savings (up to 7−11 times) and reduction of carbon dioxide emissions (up to 11 times) at different ratios of conversion and recycle. The results provide evidence that CD is a very attractive process intensification technique which brings substantial energy savings, more efficient isobutene feed utilization, and reduction of greenhouse gas emissions.

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Notes

The authors declare no competing financial interest.

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