HYDROGEN AND OCTANE BOOSTING THROUGH A NOVEL CONFIGURATION CONSISTS OF ISOTHERMAL AND MEMBRANE NAPHTHA REFORMING REACTORS -A COMPARATIVE STUDY

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Abstract

The increasing demand for hydrogen and high octane gasoline in refineries can be addressed via utilizing alternative configurations for conventional catalytic naphtha reactors (CTR). In this regard, two case studies for a combination of isothermal and tubular membrane reactors are investigated in naphtha reforming process. The isothermal reactors are fabricated as a multi tubular reactor in a furnace. Some key parameters such as aromatic and hydrogen production rates and the aromatic content of reformate are investigated and some guidelines are proposed for the selection of a proper combination according to the desired aim of production. The simultaneous enhancement in products yield due to applying the Pd-Ag membrane layer and a slight temperature drop under an isothermal circumstance are achieved. The modeling results show that the combination of tubular membrane-isothermal-tubular membrane (MIM) reactors is a promising configuration for aromatic and hydrogen enhancement as well as achieving a desired aromatic content of the reformate.

Keyword: Octane boosting; In-situ hydrogen removal; Isothermal configuration; Membrane reactor; Hydrogen production; Catalytic naphtha reforming.

1. Introduction

The general trend throughout refinery complexes has been to up bring the origin feedstock (crude oil) and produce more products from each barrel of petroleum and to process those products in different ways to meet the specifications for use in modern engines. In fact, an oil refinery incorporates a vast variety of units such as Atmospheric and Vacuum Distillations, Visbreaking, Isomax, Coking, FCC and Catalytic Naphtha Reforming. Among all, catalytic naphtha reforming has a history of 60 years and plays a significant role in the refineries [1].

1.1. Catalytic naphtha reforming

Catalytic naphtha reforming maintains its position as a major process in the petroleum refinery. Catalytic reforming provides a key link between the refining and petrochemical industries through its effective production of aromatic compounds (BTX, i.e. Benzene, Toluene, Xylenes) [2]. More over the naphtha reforming supplies the demanded gasoline and hydrogen [3,4]. This process involves the reconstruction of low-octane hydrocarbons in the naphtha into more valuable high-octane gasoline components without changing the boiling point range [5,6].

Considering the above issues, this process has been under continuous study and evolution by diversity of researchers. Complete lists of such investigations were provided in our previous publications [7-9].

1.1.1. Naphtha

Naphtha and reformate are complex mixtures of paraffins, naphthenes, and aromatics in the C_5–C_{12} range. Most of Naphtha sources is obtained from overhead of main distillation column of refineries, this type of naphta is called strait run naphtha. Other naphtha suppliers such as coker unit, visbreaker unit and fluid catalytic cracking unit (FCC) also produce coker naphtha, visbreaker naphtha and FCC naphtha respectively [10-16]. Naphthas of different origin contain small amounts of additional compounds containing elements such as sulfur and nitrogen. Generally, naphtha constitutes 15-30% of the crude oil. The number of detectable individual compounds in naphthas ranges typically from 100–300,

but these are harsh to follow individually and it is sufficient for the refiner engineers just to know about the group concentrations of PNA (paraffin, naphthene, aromatic) in order to evaluate the quality of the final products (research octane number). Usual straight-run medium naphtha contains 40-70 wt % paraffins, 20-50 wt % naphthenes, 5-20 wt % aromatics and during the catalytic reforming most of the low octane naphthenes and paraffines are converted into the high valuable aromatic compounds [5].

1.1.2. Aromatic

The high concentration of aromatics in reformates is a valuable feedstock of benzene, toluene, and particularly xylenes in the petrochemical usages [5].

Aromatics have the general formula C_nH_{2n-6} and contain one or more polyunsaturated rings (conjugated double bonds). These benzene rings can have paraffinic side chains or be coupled with other naphthenic or aromatic rings. The reactivity of the unsaturated bonds make the C_6, C_7, and C_8 aromatics or BTX (benzene, toluene, xylenes) important building blocks for the petrochemical industry. Aromatics have high octane numbers always above 100. Basically, an increase in the octane number of the reformate can best be obtained by aromatic production. Based on the available evidences throughout the literature the research octane number (RON) has a linear relation with the weight fraction of aromatic compounds in the reformate [17-20]. Hence, attempts are made to enhance the aromatic production rate in the refineries. What is more, the drive to eliminate the use of MTBE as an oxygenate component in the gasoline pool and the subsequent lose in the octane number have forced the refineries to replace this lost by increasing other high octane aromatics [5].

1.1.3. Hydrogen

In addition to high octane gasoline production (or higher aromatic production), a large quantity of required hydrogen all over the refinery complex is supplied by the reformers. Hydrogen is mainly used for hydro processing in the refinery. Furthermore, there is a growing concern about energy supply security owing to the expected increase of global energy demand. The results of global energy scenarios of IEA's Energy Technology Prospective and the WETO H_2 scenarios of the European Commission show the emergence of a considerable hydrogen demand until 2050, provided that very optimistic developments of hydrogen production and end-use technologies are assumed. Hence, the increasing in hydrogen demand will eventually lead to a boost in its manufacturing capacity [21]. In this regard, hydrogen can be nominated as an indispensable source of energy in the future. Recent progress in fuel cell technology makes it possible to envisage a major role of hydrogen in the future energy system. Typical hydrogen recovery processes include pressure-swing adsorption (PSA), membrane separation, especially metal membrane separation as one of the most cost-effective and promising methods for pure hydrogen production, and cryogenic separation [4,22-24]. Therefore, some improvements are observed in both the processing and equipment pieces of the technology as well as the catalyst component owing to the importance of the catalytic naphtha reforming process (hydrogen and high octane gasoline production) in the refinery [5]. An extensive literature review about naphtha reforming can be found in the previous publications [7,8,25,26].

1.2. Membrane reactor

The potential of membranes for gas separation has been known for more than 30 years. The first large-scale commercial application of membrane gas separation was the separation of hydrogen from nitrogen, methane and argon in ammonia purge gas stream [27]. During this relatively short time, significant development in membrane science has been come to stage from academic and industrial viewpoints [28-30] and studies are still in progress. Two groups of polymeric and inorganic membranes are discussed, but majority of investigations have been concentrated on the inorganic membrane reactors because of their excellent thermal stability under high reaction temperatures [32]. It is commonly accepted that using membrane technology in the conventional plants drives toward greater economic and environmental efficiency [53].

In many hydrogen-related reaction systems, Pd-alloy membranes on a stainless steel support were used as the hydrogen-permeable membrane [33]. It is also well known that the use of pure palladium membranes is hindered by transition from the α-phase to the β-phase at temperatures below 300°C, which depends on the hydrogen concentration in the metal. This phenomenon leads to distortion of the metal and lattice [34,35].

For endurance enhancement of the commercial Pd membranes, the pd-alloy membranes such as Pd-Ag, Pd-Cu and Pd-Au is used [36]. Alloying the palladium, especially with silver, reduces the critical temperature for embitterment and results to an increase in the hydrogen permeability. Okazaki et al. [37] showed that the durability of Pd-Ag membrane in comparison to Pd membrane was improved and showed the prevention of lattice expansion by alloying with more than 20% of silver. In other work, the highest hydrogen permeability was detected 23wt% of silver [38]. Peters et al. [39] examined the stability of the membranes by experiments. They studied the hydrogen permeation and the stability of tubular palladium alloy (Pd-23%Ag) composite membranes at elevated temperatures and pressures.

Briefly, Palladium-based membranes have been used for decades in hydrogen extraction because of their high permeability and good surface properties and this fact that palladium, like all metals, is 100% selective for hydrogen transport [40]. The palladium-copper [41], palladium-silver [42-46] were used for different processes. Rahimpour and Ghader proposed Pd–Ag membrane and Pd membrane reactors for methanol synthesis [38,47]. Tosti *et al.* [48] described different configurations of palladium membrane reactors used for separating ultra pure hydrogen. Nair *et al.* [49] recently carried out an analysis of conventional Pd and Pd/Ag membranes. Damen and coworkers model four configurations of the membrane reactor with Aspen plus to determine its thermodynamic and economic prospects [50]. These properties cause Pd-based membranes such as Pd-Ag membranes to be attractive to apply in petrochemical gases.

One apparent opportunity that would seem to match nicely with the current feature of membrane is the catalytic naphtha reformers in the refineries [27,51]. Membrane can be used effectively to increase hydrogen production and boost the octane number of the produced gasoline through this unit.

1.3. Objective

The underlying goal of this study is to investigate the performance of a combination of isothermal and tubular membrane reactors in naphtha reforming process. Two cases, Case (I) with one tubular membrane reactor and Case (II) with two tubular membrane reactors, are investigated in this study and some guidelines are proposed ultimately for the selection of the most proper combination according to the desired target of production. Here, M and I represent Membrane tubular and Isothermal reactors, respectively. Since in the previous study [8], the hydrogen production rate decreased in isothermal configuration, the combination of isothermal and tubular membrane reactors is proposed as a novel configuration and a remedy for this undesired phenomenon.

2. Process description

2.1. Conventional tubular reactor (CTR)

The catalytic naphtha reforming process by CTR configuration has been extensively discussed in the previous publication [52]. A simplified process diagram for CTR is shown in Fig.1.
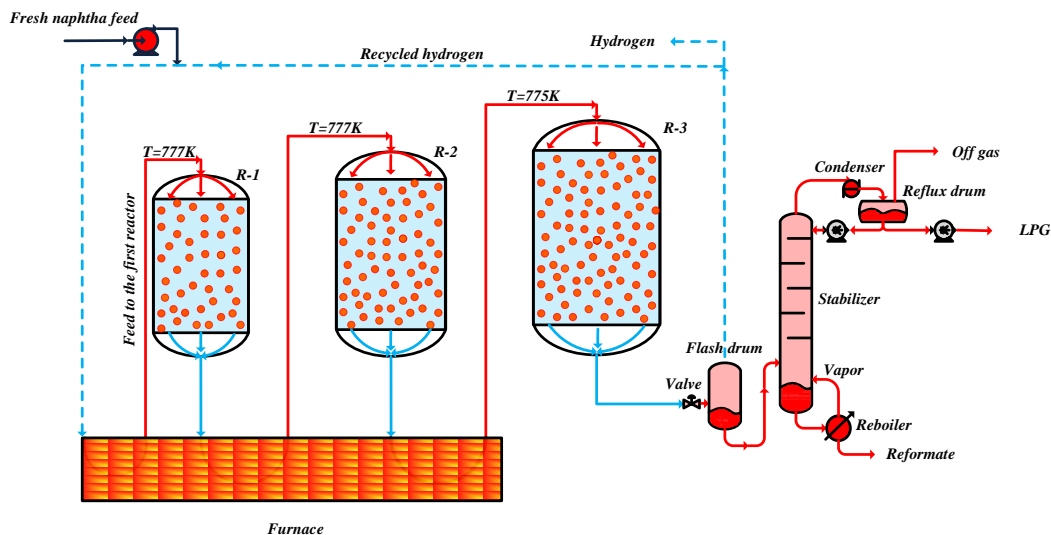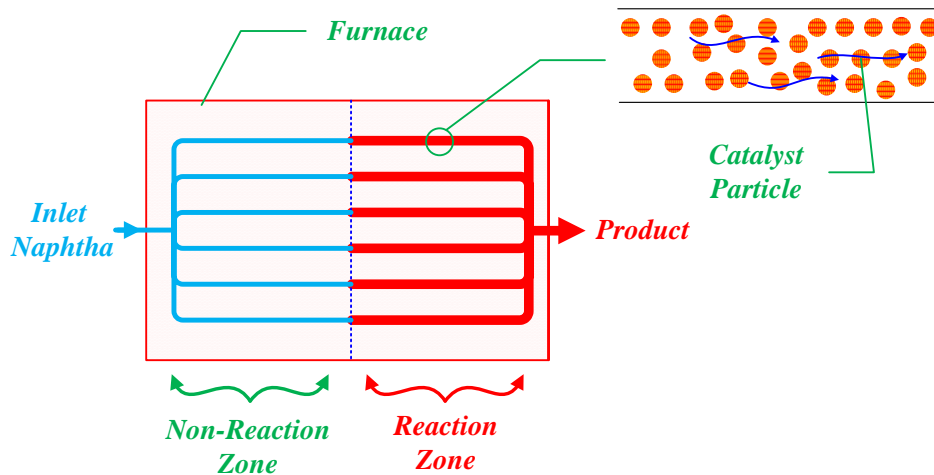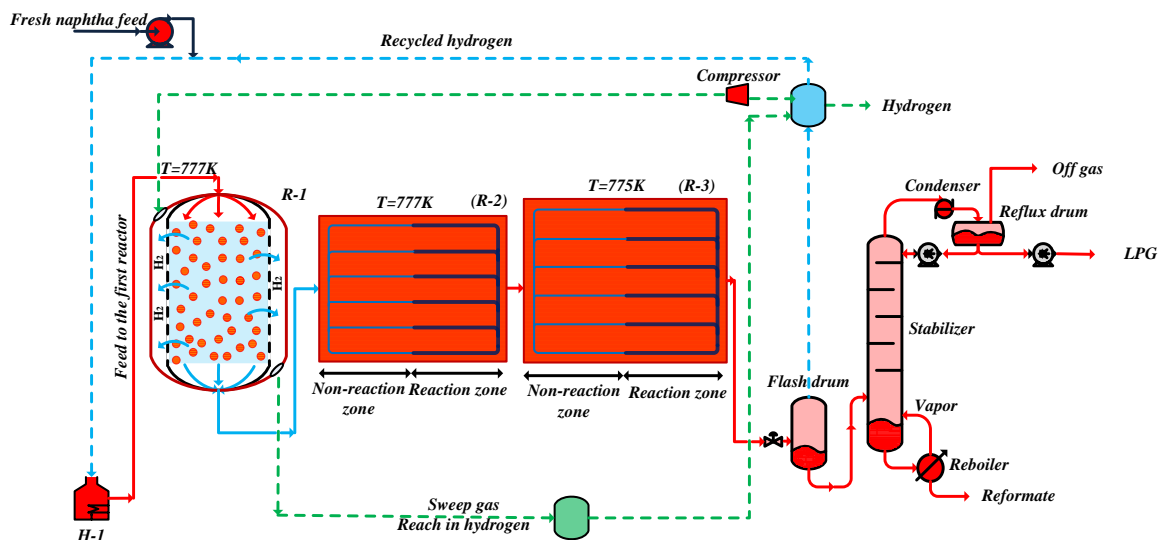

Fig.1 A simplified process diagram for CTR.

2.2. A combination of isothermal an tubular membrane reactors

In the isothermal configuration, the reactor is fabricated as a multi tubular reactor inside a furnace. The furnace consists of the non-reaction section where the inlet naphtha feed is preheated by parallel tubes and the reaction section where the chemical reactions take place in a multi tubular reactor which are packed by catalysts. A conceptual design for multi tubular reactors in a furnace is depicted in Fig.2 (a). Since the temperature is maintained at 777K by the furnace, reactors operate under an isothermal condition. Cases (I) and (II) are investigated in this study where the former one is a combination of two isothermal reactors and one tubular membrane reactor while the latter one is a combination of one isothermal reactor and two tubular membrane reactors. The Pd-Ag membrane layer is assisted in tubular reactors to enhance the production rates of main products according to the thermodynamic equilibrium. Schematic process diagrams for a combination of isothermal and tubular membrane reactors for MII and MIM combinations are illustrated in Fig.2 (b)-(c).

2a

2b

2c

Fig.2 Schematic process diagram of (a) for multi tubular reactors in a furnace (b) combination of isothermal and tubular membrane reactors for MII and (c) MIM

3. THE KINETIC OF REACTIONS

In order to verify the feedstock or product qualities, it is often sufficient for the process engineers to know the PONA (paraffin, olefin, naphthene and aromatic) group concentrations. Our available process data sheets from three domestic refineries are reported based on PNA [5,53]. Therefore, a simplified model based on the Smith's model [54], with four predominant reactions, is considered to reduce the complexity of naphtha feed. The related reactions are as follows:

- Dehydrogenation of naphthenes to aromatics
Naphthenes (C_nH_{2n})↔Aromatics (C_nH_{2n-6})+$3H_2$ $\Delta H = 71038.06 (kj/kmol\ H_2)$ (1)

- Dehydrocyclization of paraffins to naphthenes
Naphthenes (C_nH_{2n})+H_2↔Paraffins (C_nH_{2n+2}) $\Delta H = -36953.33 (kj/kmol\ H_2)$ (2)

- Hydro cracking of naphthenes to lower hydrocarbons
Naphthenes (C_nH_{2n}) + $n/3H_2$→Lighter ends (C_1–C_5) $\Delta H = -51939.31 (kj/kmol\ H_2)$ (3)

- Hydro cracking of paraffins to lower hydrocarbons
Paraffins (C_nH_{2n+2}) + $(n-3)/3H_2$→Lighter ends (C_1–C_5) $\Delta H = -56597.54 (kj/kmol\ H_2)$ (4)

The corresponding reactions' rates and their constants have been reported in previous publications [25].

4. Mathematical modeling, numerical solution and model validation

The corresponding mass and energy balance equations as well as the pressure drop correlation [55] and the Sievert's law correlation [56] are presented in Table 1. Furthermore, some useful auxiliary correlations are used in the developed model.

Table 1 Mass and energy balances.

Isothermal reactor

$$D_{ej}\left(\frac{\partial^2 C_j}{\partial z^2}\right) - \frac{\partial(u_z C_j)}{\partial z} + \rho_B a \sum_{i=1}^{m} v_{ij} r_i \tag{5}$$

$$= \varepsilon \frac{\partial C_j}{\partial t} \quad j=1,2,...,n \quad i=1,2,...,m$$

$$C_T C_v \varepsilon \frac{\partial T}{\partial t} = RT \frac{\partial C_T}{\partial t} + k_{eff}\left(\frac{\partial^2 T}{\partial z^2}\right) - u_z C_p \frac{\partial T}{\partial z} + \rho_b \sum_{i=1} r_i \Delta H_i \tag{6}$$

Membrane reactor

Fluid phase (Reaction side)

$$D_{ej}\left(\frac{\partial^2 C_j}{\partial z^2}\right) - \frac{\partial(u_z C_j)}{\partial z} + \rho_B a \sum_{i=1}^{m} \nu_{ij} r_i \tag{7}$$

$$-\begin{cases} \dfrac{P_{per}}{A_{c_1}} J_{H_2} & j = H_2 \\ 0 & j \neq H_2 \end{cases} = \varepsilon \frac{\partial C_j}{\partial t} \quad j = 1,2,...,n \quad i = 1,2,...,m$$

$$C_T C_v \varepsilon \frac{\partial T}{\partial t} = RT \frac{\partial C_T}{\partial t} + k_{eff}\left(\frac{\partial^2 T}{\partial z^2}\right) - u_z C_p \frac{\partial T}{\partial z} + \rho_b \sum_{i=1} r_i \Delta H_i \tag{8}$$

$$+ J_{H_2} \frac{\beta P_{per}}{A_{c_1}} (H_{H_2}^t - \gamma_{H_2}) + \frac{P_{per} U}{A_{c_1}} (T^s - T)$$

$$\beta = U_{HVS}(P_{H_2}^t - P_{H_2}^s) = \begin{cases} +1 & P_{H_2}^t \geq P_{H_2}^s \\ -1 & P_{H_2}^t < P_{H_2}^s \end{cases} \tag{9}$$

U_{HVS} : Heaviside Function

$$\gamma_{H_2} = (H_{H_2}^t - H_{H_2}^s) U_{HVS}(P_{H_2}^t - P_{H_2}^s) + H_{H_2}^s = \begin{cases} H_{H_2}^t & P_{H_2}^t \geq P_{H_2}^s \\ H_{H_2}^s & P_{H_2}^t < P_{H_2}^s \end{cases} \tag{10}$$

Fluid phase (Sweep gas side)

$$D_{ej}\left(\frac{\partial^2 C_j}{\partial z^2}\right) - \frac{\partial(u_z C_j)}{\partial z} + \begin{cases} \dfrac{P_{per}}{A_{c_1}} J_{H_2} & j = H_2 \\ 0 & j \neq H_2 \end{cases} = \varepsilon \frac{\partial C_j}{\partial t} \quad j = 1,2,...,n \quad i = 1,2,...,m \tag{11}$$

$$C_T C_v \varepsilon \frac{\partial T^s}{\partial t} = RT^s \frac{\partial C_T}{\partial t} + k_{eff}\left(\frac{\partial^2 T^s}{\partial z^2}\right) - u_z C_p \frac{\partial T^s}{\partial z} \tag{12}$$

$$- J_{H_2} \frac{\beta P_{per}}{A_{c_2}} (H_{H_2}^t - \gamma_{H_2}) - \frac{P_{per} U}{A_{c_2}} (T^s - T)$$

Hydrogen permeation rate

$$J_{H_2} = \frac{Q_0 \exp\left(-\dfrac{E_{H_2}}{RT}\right)}{\delta_{H_2}} \left(\sqrt{P_{H_2}^{tube}} - \sqrt{P_{H_2}^{shell}}\right) \tag{13}$$

$$Q_0 = 1.65 \times 10^{-5} mol m^{-1} s^{-1} kPa^{\frac{-1}{2}}, E_{H_2} = 15.7 kjmol^{-1}$$

Additional relations

$$P_{per} = \pi D_1 \tag{14}$$

$$A_{c_1} = \frac{\pi}{4} D_1^2 \tag{15}$$

$$A_{c_2} = \frac{\pi}{4}(D_H^2 - D_1^2) \tag{16}$$

Boundary conditions

$$z = 0: \ C_j = C_{j0}, \ T = T_0 \tag{17}$$

$$z = L: \ \frac{\partial C_j}{\partial z} = 0, \ \frac{\partial T}{\partial z} = 0 \tag{18}$$

Ergun equation (Pressure drop)

$$\frac{dP}{dz} = \frac{150\mu}{\phi_s^2 d_p^2} \frac{(1-\varepsilon)^2}{\varepsilon^3} \frac{Q}{A_c} + \frac{1.75\rho}{\phi_s d_p} \frac{(1-\varepsilon)}{\varepsilon^3} \frac{Q^2}{A_c^2} \tag{19}$$

Steady-state simulation of the reactors is achieved by setting all time variations of states to zero and also considering fresh catalysts. The set of ODEs (energy and mass balance equations in tubular reactor) as well as algebraic equations (the auxiliary correlations, kinetics and thermodynamics of the reaction system) are integrated by a modified Rosenbrock formula of order two.

A comparison between the achieved results from proposed model and conventional tubular packed-bed reactors under the steady-state condition has been reported in Table 2. As seen, there is an acceptable agreement between the predicted results and the plant data. Analyses of the components (paraffin, naphthene and aromatic) are performed by PONA test apparatus. The PONA test is a GC apparatus which operates with Helium as a carrier gas. The system is composed of three parts including split injector, temperature programmed oven and the ionization detector. The analysis time is around one hour and a half. The components are identified based on the peaks which are appeared by the GC. In order to detect all the individual compounds, more complex temperature program and also time are require. For the process engineer, it is often sufficient to know the PONA group concentration in order to verify the feedstock or product qualities and the least time-consuming by GC methods. This test is usually taken monthly based on our data sheets from the domestic refinery [5,53].

Table 2 Comparison between model prediction and plant data for fresh catalyst.

Reactor No.	Inlet temperature (K)	Inlet pressure (Kpa)	Catalyst distribution (wt %)	Input feedstock (Mole %)	
1	777	3703	20	Paraffin	49.3
2	777	3537	30	Naphthene	36
3	775	3401	50	Aromatic	14.7

	Outlet temperature (K)			Aromatic in reformate (Mole %)			
No.	Plant	CTR	MII	MIM	plant	CTR	MII	MIM
1	722	727.30	729.82	729.82	–	34.67	34.85	34.84
2	753	750.98	777.00	777.00	–	47.19	54.02	54. 03
3	770	770.53	775.00	772.04	57.70	56.18	63.10	63.66

5. Results and discussion

The modeling results of various combinations are investigated in the following figures in order to recognize the best configuration for catalytic naphtha reforming process.

5.1. The combination of a tubular membrane reactor and two isothermal reactors (Case I)

In order to investigate the performance of case (I), the variation of some key parameters such as aromatic and hydrogen production rates, H_2/HC molar ratio, the aromatic content of reformate are studied along the reactors.

The obtained aromatic compounds from the catalytic reformers are used for adjusting octane number of gasoline pools. Aromatics are considered to have octane number of more than 100 [5]. Moreover, aromatics are used as intermediate products for production of thousands of materials by the petrochemical complexes. On the other hand, the produced hydrogen from the catalytic naphtha reformers is used for removing sulfur and nitrogen compounds and producing lighter fuels in the hydrotreating and hydrocracking units [4]. The aromatic and hydrogen production rates along three possible combinations of case (I) and CTR (also named as TTT here) are depicted in Fig.3 (a)-(b). As seen, the aromatic production rate increases considerably along IMI in comparison with CTR. Since the temperature of multi tubular reactors in the isothermal configuration is maintained constant via furnaces, the reaction rates and consequently the aromatic and hydrogen production rates by the dehydrogenation reaction (eq.1) increase considerably at higher temperatures. The aromatic production rate in the outlet of the first reactor in IIM and IMI configurations is higher than even the outlet aromatic production rate from the second reactor in CTR. About 82% of total aromatic production is achieved in the first reactor of IIM and IMI. Although higher aromatic production rate is achieved in IMI (about 800 *kg/h* compared with CTR), the hydrogen production rate via MII is superior compared with the other

configurations in Case (I). Providing a heating source (high temperature) for the first reactor where the naphthene and paraffin concentrations are high proceeds the irreversible reactions (eq.3 and 4) and turns a portion of produced hydrogen into the light ends. In MII configuration, lower temperature profile in the tubular membrane reactor than the isothermal one as well as assisting the membrane layer in the first reactor of MII combination avoids the unfavorable hydrogen consumption via these two reactions. Consequently, higher hydrogen yield is achieved in MII. Fig.3 (b) shows that 100% of total hydrogen production is achieved by applying just one isothermal configuration (the first reactor). This means a huge saving in the initial cost of investment form neglecting the second and the third reactors and providing expensive catalyst (Catalyst contains Pt alloy). However, a cost evaluation between lower hydrogen production (about 9 *kmol/h* compared with the CTR) and saving in the operational and initial costs of investment should be considered before making any decision.
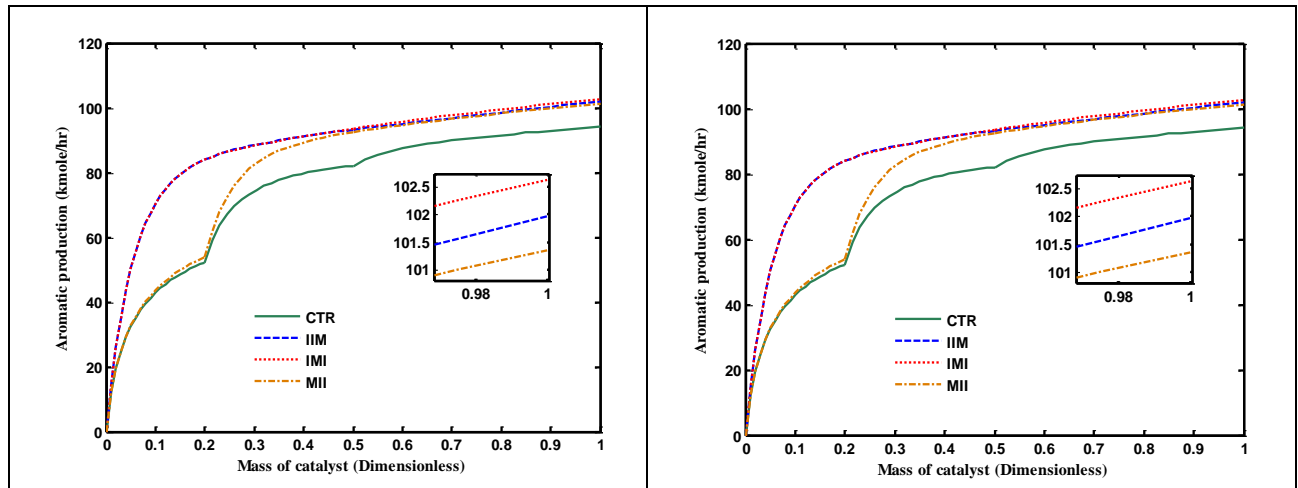
Fig.3 (a) The aromatic and (b) hydrogen production rates along the three possible configurations of case (I) and CTR
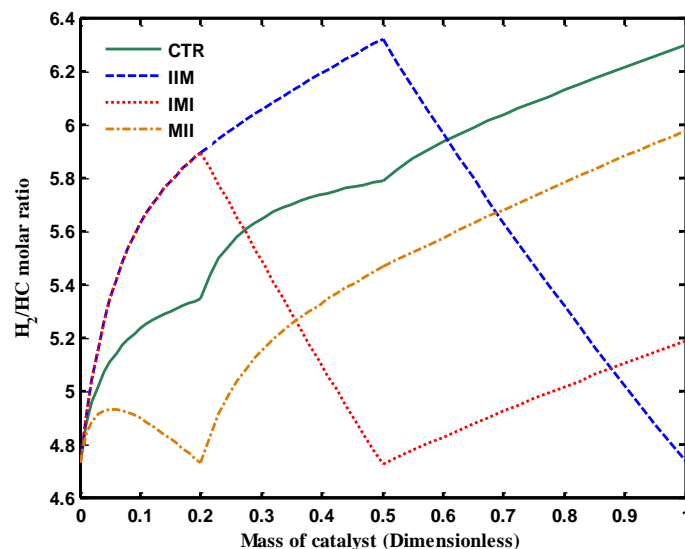

Fig.4 H_2/HC molar ratio along CTR and Case (I)

The H_2/HC molar ratio is a key parameter to control the catalyst load and catalyst deactivation in naphtha reforming process as shown in Fig.4. The catalyst deactivation decreases considerably at high H_2/HC molar ratio however higher aromatic and hydrogen yield are achieved at low H_2/HC molar ratios therefore lower H_2/HC molar ratio is preferred although this is always a trade-off with the catalyst stability [5]. The H_2/HC molar ratio increases gradually along CTR owing to continuous hydrogen production in the reaction side. Assisting a membrane layer in a tubular reactor extracts the excessive amount of produced hydrogen from the reaction side and enhances the production rates. It is worth mentioning that the permeation side pressure is adjusted in tubular membrane reactor in

order to maintain the H_2/HC molar ratio above 4.73. Increasing/decreasing trends (the maximum points) are observed in the reactors of Case (I) owing to applying the Pd-Ag membrane layers. A remarkable increase in the H_2/HC molar ratio along the first and the second reactors of IIM configuration is due to a large amount of hydrogen production as well as paraffin consumption in two subsequent isothermal reactors.

The light ends production rate and the aromatic content of reformate are illustrated in Fig.5 (a)-(b). The light ends production rate in the isothermal configurations of Case (I) including IIM, IMI and MII is remarkably higher than CTR owing to higher temperature profile in isothermal configuration that leads to higher reaction rates of hydrocracking of naphthenes and paraffins to lighter fractions. The light ends are valuable products which are used as the main source of LPG in the refineries. LPG is withdrawn from the top section of stabilizer. The aromatic content of the reformate increases considerably in isothermal configurations in Case (I) in comparison with CTR mainly due to considerably higher aromatic production rate in isothermal configurations (see Fig. 3(a)). The highest octane gasoline can be achieved in IMI and IIM owing to higher aromatic content of reformate compared with the other configurations. By adopting IMI configuration, the total area of membrane decreases approximately 24% in comparison with the IIM.
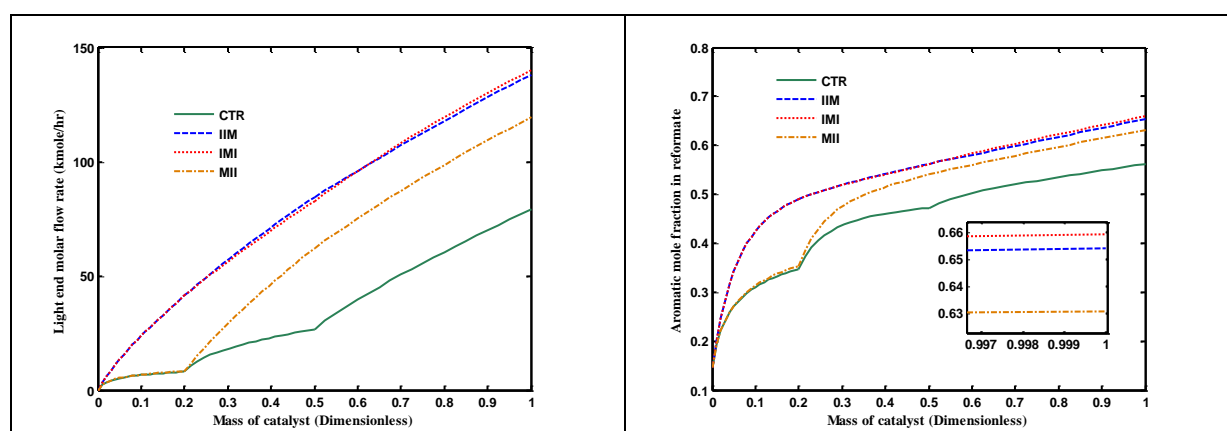

Fig.5 (a) The light ends production rate (b) the aromatic content of reformate along CTR and Case (I)

The above mentioned results are provided in Table 3. According to the results, the MII configuration is selected among the possible combinations of Case (I). The criteria for the selection of the best combinations are the aromatic, hydrogen and reformate production rates and the aromatic content of the reformate. These parameters proposed the MII configuration as the most proper combination.

Table 3 – The achieved results for configurations of Case (I) and conventional reactor (TTT).

No.	Configuration	Aromatic production ($\frac{kmol}{h}$)	Hydrogen production ($\frac{kmol}{h}$)	Reformate production ($\frac{kmol}{h}$)	Aromatic mole percent in the reformate
1	TTT	94.2819	235.1570	237.6068	56.1827
2	IIM	101.9685	227.1891	215.8360	65.4110
3	IMI	102.6205	228.6778	215.1476	65.9234
4	MII	101.3591	237.2135	222.7649	63.1029

5.2. A combination of two tubular reactors and one isothermal reactors (Case II)

The other alternative configuration is to apply the combination of two tubular membrane reactors and one isothermal reactor (Case II) in naphtha reforming process. In this regard, the aromatic and hydrogen production rates along Case (II) and three tubular membrane reactors (MMM) are illustrated in Fig.6 (a)-(b). The aromatic production rate in IMM and MIM are higher than the other configurations. Since the naphthenes dehydrogenation reaction takes place predominantly in the first and second reactors, operating under the isothermal condition in these reactors can be in favor of aromatic production. Furthermore, the Pd-Ag membrane layer in tubular reactors enhances the aromatic production

rate. By choosing the MIM configuration, the membrane area reduces to 7.4 m² compare with the IMM one.

Since the first reactor in IMM configuration is fabricated inside a furnace (i.e., operating under isothermal condition), the temperature profile in IMM is higher than the other combinations and consequently more hydrogen turns into lighter ends according to equations 3 and 4. Therefore, the hydrogen production rate in IMM is the lowest among the other combinations of Case (II). However, the application of the Pd-Ag membrane layer and also fabricating the second or the third reactor inside a furnace compensates a decrease in hydrogen production rate in isothermal configurations.
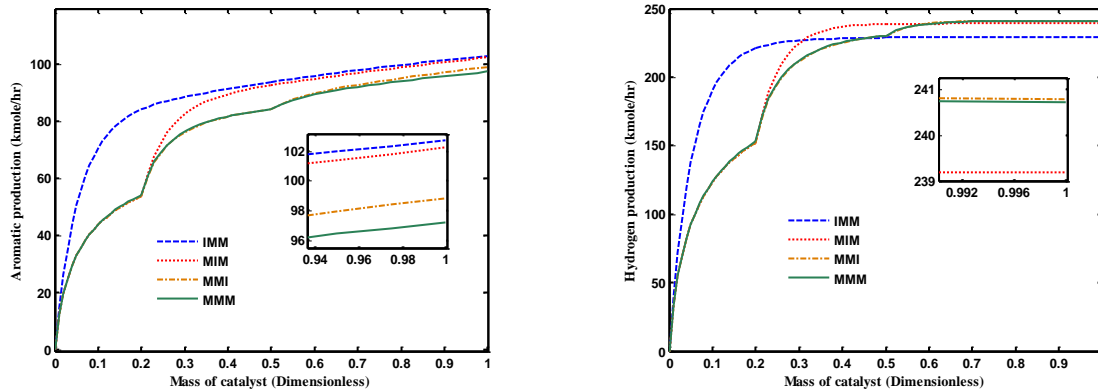
Fig.6 (a) The aromatic and (b) hydrogen production rates along Case (II) and three tubular membrane reactors (MMM)

The aromatic content of reformate is expressed in Fig.7. The aromatic content of reformate in IMM is considerably higher than the other combinations. According to the reported results in Table 4, MIM configuration is the best combination of Case (II).
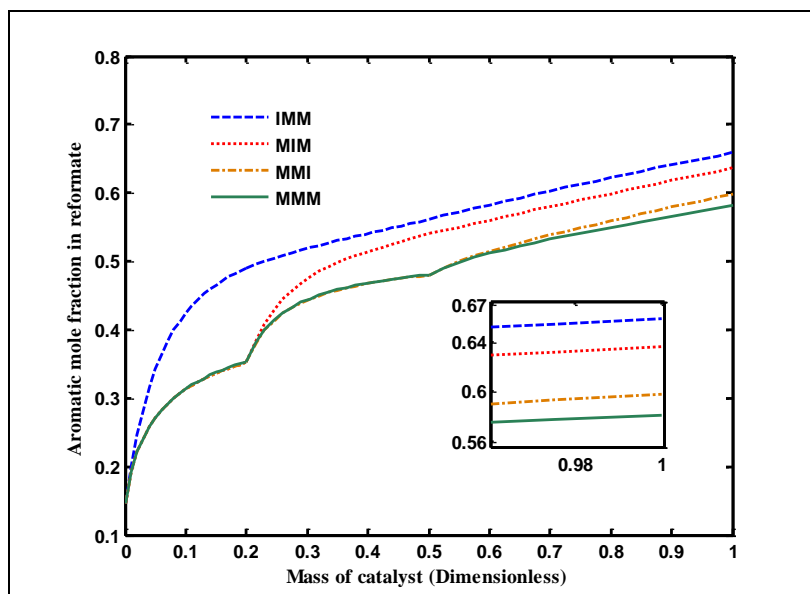

Fig.7 The aromatic content of reformate along Case (II) and MMM

Table 4 – The achieved results for configurations of Case (II) and membrane reactor (MMM).

No.	Configuration	Aromatic production $(\frac{kmol}{h})$	Hydrogen production $(\frac{kmol}{h})$	Reformate production $(\frac{kmol}{h})$	The aromatic mole percent in reformate
1	MMM	97.2053	240.7037	234.4507	58.1859
2	IMM	102.7059	229.3228	215.3892	65.8890
3	MIM	102.2119	239.1858	222.1570	63.6594
4	MMI	98.8211	240.7684	230.7572	59.8175

5.3. A COMPARISON BETWEEN THE PERFORMANCES OF MII AND MIM

A comparison between the performances of MII and MIM is provided in the following graphs:

The hydrogen production rate and aromatic molar flow rate along the third reactors of MII and MIM are demonstrated in Fig.8 (a)-(b). The in situ hydrogen removal via the Pd-Ag membrane layer in tubular reactors shifts the dehydrogenation reaction (eq.1) to the product side (hydrogen and aromatic) in accordance with the Le Chatelier's principle and enhances the aromatic and hydrogen production rates. Higher hydrogen production rate in MIM than MII can be justified by less hydrogen conversion to lighter ends in MIM. Owing to fabricating two isothermal reactors in MII, the temperature drop in MII is considerably lower than MIM therefore the reaction rates and as a consequence the conversion of hydrogen to lighter ends in MII is higher than MIM.
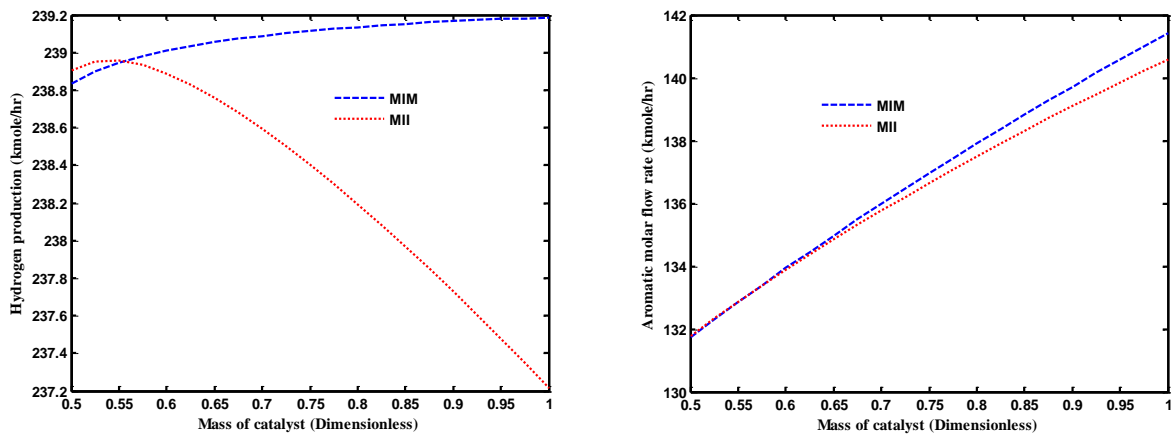

Fig.8 (a) The hydrogen production rate and (b) aromatic molar flow rate along MII and MIM

The reformate consists mainly of paraffinic and aromatic hydrocarbons while the large part of naphthenes is consumed in the reaction. The purpose of catalytic reforming is primarily to increase the octane number of the naphtha feedstock to a level that makes the reformate product as suitable as a gasoline blend stock. The reformate molar flow rate and the aromatic content of the reformate are investigated in Fig.9 (a)-(b). The aromatic content of the reformate in MIM is higher than MII.

A comparison between the performances of MII and MIM indicates that the MIM configuration is superior. Thus, MIM is selected among all the possible combinations of Cases (I) and (II). The modeling results of MIM and MII combinations are summarized in Table 5.
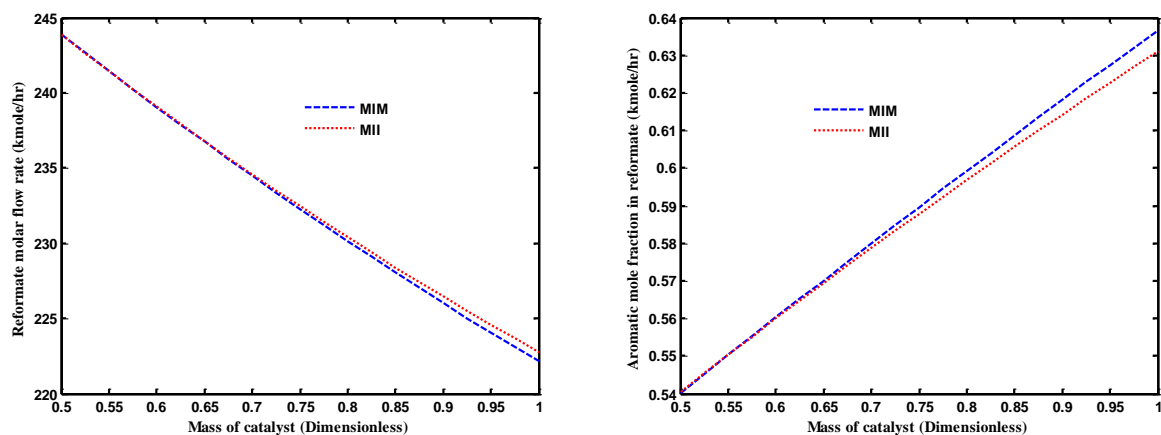

Fig.9 (a) The reformate molar flow rate (b) the aromatic content of the reformate along MII and MIM

Table 5 A comparison between the aromatic, hydrogen production rates and the aromatic content of reformate in the MIM, MII and TTT.

No.	Configuration	Aromatic production $(\frac{kmol}{h})$	Hydrogen production $(\frac{kmol}{h})$	Reformate production $(\frac{kmol}{h})$	The aromatic mole percent in reformate
1	TTT	94.2819	235.1570	237.6068	56.1827
2	MIM	102.2119	239.1858	222.1570	63.6594
3	MII	101.3591	237.2135	222.7649	63.1029

5.4. General guidelines

Some guidelines are provided in this study (Fig.10 (a)-(d)) to select the most proper combination in accordance with the main desired goal of production.

If the hydrogen production becomes vital as the main goal of naphtha reforming process, MMI is the best choice among eight proposed combinations (see Fig.10 (a)). Therefore, MMI configuration can be proposed as a novel configuration for satisfying the increasing hydrogen demand in refineries for sulfur and nitrogen compounds removal from gasoline and diesel. Moreover, lighter fuels production can be properly addressed via MMI configuration. This configuration is more reliable to be applied by the process engineers on account of diminishing the membrane layer area and its maintenance costs in contrast with the MMM one.

On the other hand, if the aromatic production is the target of naphtha reforming process to increase the gasoline octane number, the selection can be varied between IMM, IMI and MIM (see Fig.10 (b)).

TTT (conventional tubular reactor) is obviously the best choice for the reformate production rate (Fig.10 (c)) because the reformate production rate in isothermal configurations decreases compared with TTT owing to more conversion of naphthenes and paraffins to lighter ends (as a result of higher temperature profile).

The purpose of catalytic reforming is primarily to increase the octane number of the naphtha feedstock to a level that makes the reformate product suitable as a gasoline blend stock. IMI is definitely the most proper configuration for the purpose of high aromatic content of reformate according to Fig.10 (d). As high concentration of aromatics in reformates offers high octane ratings in addition to a rich source of benzene, toluene and particularly xylenes, IMI configuration can properly address these requirements.

A comparison between the aromatic and hydrogen production rates and the aromatic content of reformate in eight possible combinations are reported in Table 6. A proper decision for the selection of the most suitable combination in accordance with the desired and the state-of-the-art goal of production in the refinery can be made based on the above figures and Table 6.
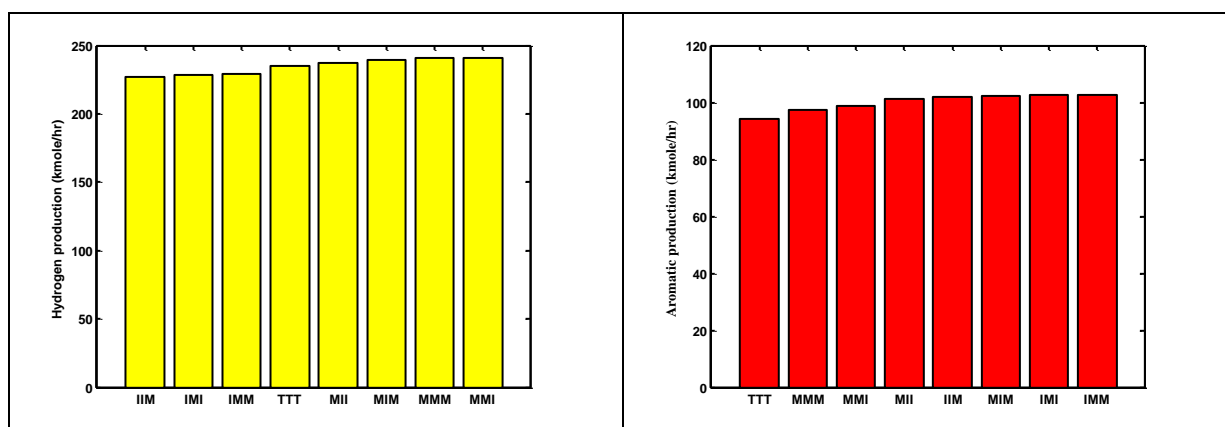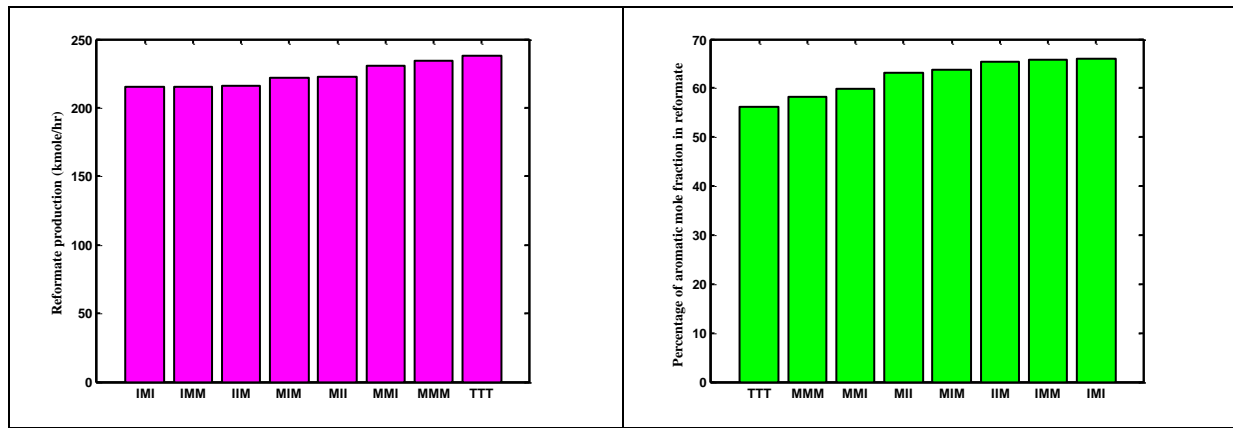
Fig.10 (a) Hydrogen production rate (b) the aromatic production rate (c) the reformate production rate (d) aromatic content of reformate along eight combinations

Table 6 The achieved results from the eight possible configurations for conventional catalytic naphtha reactor.

No.	Configuration	Aromatic production ($\frac{kmol}{h}$)	Hydrogen production ($\frac{kmol}{h}$)	Reformate production ($\frac{kmol}{h}$)	The aromatic mole percent in reformate
1	TTT	94.2819	235.1570	237.6068	56.1827
2	IMM	102.7059	229.3228	215.3892	65.8890
3	MIM	102.2119	239.1858	222.1570	63.6594
4	MMI	98.8211	240.7684	230.7572	59.8175
5	MMM	97.2053	240.7037	234.4507	58.1859
6	IIM	101.9685	227.1891	215.8360	65.4110
7	IMI	102.6205	228.6778	215.1476	65.9234
8	MII	101.3591	237.2135	222.7649	63.1029

6. Conclusions

In this study, a combination of isothermal and tubular membrane reactors is proposed as a novel configuration for catalytic naphtha reforming process. In the isothermal confi-guration, reactors are fabricated as a multi tubular reactor inside a furnace where the temperature is maintained constant and the reactor operates under an isothermal condition. Six possible combinations in addition to the conventional (TTT) and membrane (MMM) tubular reactors are investigated and the main parameters such as aromatic, hydrogen and reformate production rates and aromatic content of reformate, etc. are considered as criteria to recognize the best combinations. The modeling results show that the combination of tubular membrane-isothermal-tubular membrane (MIM) is superior among all the possible combinations owing to achieving desirable aromatic and hydrogen production rates as well as the aromatic content of the reformate. Some guidelines are proposed ultimately for choosing the proper combination in accordance with the desired criteria. Regarding this, the modeling results propose the MMI, IMM, TTT and IMI combinations for high hydrogen, aromatic and reformate production rate and the aromatic content of reformate, respectively. The undesired decrease in hydrogen production in isothermal configurations, as previously investigated [8], is properly solved by assisting the Pd-Ag membrane layer in tubular reactors. The modeling results show that a combination of isothermal and tubular membrane reactors is an appropriate alternative for conventional reactors in naphtha reforming process however the cost evaluations of such a novel configuration should be supplemented as a future work to have an entire judgment.

Nomenclature

Parameter	Description, dimension
a	catalyst activity
A	moles of aromatic formed (kmol h^{-1})
A_c	cross-section area of reactor (m^2)
C	concentration (kmol m^{-3})
C_{j0}	inlet concentration of component j (kmol m^{-3})
C_P	specific heat capacity (kJ kmol^{-1} K^{-1})
d_p	particle diameter (m)
D_e	effective diffusivity (m^{2}s^{-1})
E_d	activation energy of catalyst (J mol^{-1})
h_f	heat transfer coefficient (W m^{-2} K^{-1})
HC	hydrocarbon (kmol h^{-1})
H_2	hydrogen (kmol h^{-1})
i	numerator
j	numerator
k_{eff}	effective thermal conductivity (W m^{-1} s^{-1})
L	length of reactor (m)
m	number of reaction
n	average carbon number for naphtha
n	number of components
P_i	partial pressure of i component (kPa)
P	total pressure (kPa)
Q	volumetric flow rate (m^{3}s^{-1})
r	radius (m)
r_i	rate of reaction for i reaction (kmol kgcat^{-1} h^{-1})
s_a	specific surface area of catalyst pellet (m^2 kg^{-1})
t	time (h)
T	temperature of gas phase (K)
T_{ref}	reference temperature (K)
z	reactor length (K)

Greek letters

ε	void fraction of catalyst bed
μ	viscosity of gas phase (kg m^{-1} s^{-1})
v_{ij}	stoichiometric coefficient of component i in reaction j
ρ_b	reactor bulk density (kg m^{-3})
ρ	density of gas phase (kg m^{-3})
ΔH	heat of reaction (kJ kmol^{-1})
ϕ_s	sphericity

Subscripts and Superscript

i	numerator for reaction
j	numerator for component
n	naphthene
p	paraffin
ss	steady state

Abbreviation

FBP	final boiling pint (°C)
IBP	initial boiling pint (°C)
CTR	conventional tubular reactor
MMM	membrane-membrane-membrane configuration
TBP	true boiling point (K)
TTT	tubular-tubular-tubular configuration (conventional tubular reactor)
WHSV	weight hourly space velocity (h^{-1})

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