Progress in spherical packed-bed reactors

Recent advances on spherical reactors for chemical and refinery industries

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Research Highlights

- All spherical reactors have been investigated from the beginning (1958) up to now.
- Several configurations of spherical packed bed reactors have been described and categorized.
- Unpacked spherical reactors are described and reviewed.
- The performance of spherical and conventional reactors has been compared.

Abstract

Given the increasing energy demands in today's word accompanied by the growing environmental concerns, the development of novel reactor configurations, which allow reducing the energy consumptions, is of considerable importance to chemical industries. The spherical geometry has been proposed as an attractive alternative to standard design of chemical reactors, as these allow for a decrease in pressure drop compared to packed beds, as well as a decrease in the costs. In this paper, a detailed review from the first paper on spherical reactors up until now on the numerical modeling and experimental analysis of spherical reactors is presented. Several configurations of spherical reactors have been described and categorized. Also, various efficient arrangements and combinations of tubular or/and spherical reactors at industrial scale are discussed. Afterward, comparisons are presented between the novel spherical reactors and conventional reactors, proving the superiority of spherical reactors in several aspects. Finally, some ideas for future research are presented. As a general conclusion, spherical reactors can be taken into consideration as a promising candidate for industrial reactors; as they are much more cost-effective than the conventional counterpart.

Keywords:

Spherical reactor; Packed-bed; Membrane; Reactor configuration; Axial-Flow; Radial-flow.

Contents

1- Introduction

Chemical industry is of great importance to the global economy, playing a key role in vital processes, ranging from the production of clean drinking water to fertilizers up to pharmaceuticals. Engineers are faced with the challenge of warranting profitability in a rapidly growing market. Slight improvements in the efficiency of manufacturing fuels and chemicals have resulted in more cost-effective and sustainable processes.

For any chemical reactor, minimizing the pressure drop is one of the most crucial concerns. Particularly, in gas-phase reactions, the species concentrations are proportional to the total pressure, and thus the reaction rates and conversion significantly decrease as the pressure drop increases through the reactor length. Additionally, the unconverted gases need to be recompressed to be recirculated in the reactor. Consequently, the pressure drop in a reactor is a key factor, which significantly affects the success or failure of a reactor design.

Conventional tubular reactors (TR) have been extensively operating at industrial scale for the production of a number of important commodities and fuels such as methanol, polyethylene, ammonia, hydrogen, naphtha, biodiesel, gasoline, etc. [1-4]. Nevertheless, they suffers from some major drawbacks such as considerable pressure drop across the bed, high manufacturing costs resulting from large wall thickness, and low production capacity [5]. Therefore, it is necessary to develop another alternative for such reactors. Recently, the idea of a spherical reactor has been proven to be an effective solution to the challange pressure drop in a chemical reactor [6]. Smaller catalyst size, lower manufacturing costs, smaller wall thickness, as well as high production capacity have also been among the main superiorities of this reactor configuration [5].

The goal of the present paper is to provide a comprehensive review on the spherical reactor concept and some of its applications in recent decades as a novel and industrially interesting reactor configuration. Statistical analysis of the relevant literatures, modeling, simulation and optimization approaches, and application of membrane and challenges of utilizing it in spherical reactors will be also reviewed. Two different configurations of the continuous packed bed spherical reactors, namely the the radial-flow and axial-flow; will be illustrated and discussed. Radial and axial flow spherical reactors will be compared with conventional tubular reactors. The remaining of the paper will take a brief look at papers related to unpacked spherical reactors. Finally, several suggestions will be proposed as a guideline for further researches.

2- The evolution of spherical reactor

The idea of using radial flow pattern in chemical reactors dates back to 1964, when Haldor Topsge Comp. proposed a radial flow cylindrical reactor to reduce pressure drop through a catalytic bed [7]. This new approach had been received much attention and many researchers studied the influence of different parameters on the efficiency of this reactor configuration [8-14]. In 1965, Cimbalinik et al. [15] considered a spherical radial flow reactor, consisting of two concentric spheres and the catalysts were placed between the two spheres. This reactor structure also appeared very interesting for the researchers and has been applied for various processes [7, 16, 17]. The concept of axial flow spherical reactors was patented by in 1961. Subsequently, many researchers have investigated this reactor configuration [18-21].

The spherical geometry of a reactor affects the operating (more specifically hydrodynamics) parameters; and thus, many scientists have been investigating this novel configuration for different reaction systems. As a result, many theoretical and experimental studies have been presented and various aspects of spherical reactors, from modeling and design to optimization and environmental concerns, have been investigated [5]. The trend of total number of published papers per year is shown in Fig. 1. As illustrated, the idea of using the novel spherical shape geometry as reaction vessel has attracted an increasing interest. More specifically, in recent years, the main portion of studies has been allocated to the packed bed (catalytic) spherical reactors.

Fig. 1

Fig. 2 presents a statistical comparison between the theoretical analysis (i.e. simulation, modeling and optimization studies) and experimental (laboratory to industrial scale) studies regarding spherical reactors. As shown, the majority of studies (89%) have been focusing on theoretical aspects of spherical reactors. This is because of the fact that computational modeling of fluid behavior has been a strong tool for the design and analysis of real scale processes, and has the potential to be applied for improving the performance of real reactors [22]. Hence, most of the previous studies have emphasized on theoretical modeling of spherical reactors.

Fig. 2

3- Continues packed bed spherical reactors

It is fairly correct to say that most of the industrial chemical reactors have a fixed or fluidized, catalytic bed design.. Packed beds are preferred because of their comparatively simplicity, which facilitate their design, construction, and operation [23].

From an engineering perspective, applying large catalyst pellets in chemical reactors is more practical, especially because they result in a lower pressure drop. Therefore, for designing such reactors, the limitation of internal diffusion through the large catalyst particles, and in commercial scale mass and heat transfer inside the reactor must be considered [16, 24]. Based on the fact that the pressure drop in a spherical reactor is lower than that in a tubular one, it offers the advantages of operating with preferably smaller catalyst pellets, higher catalyst effectiveness factor, and more significant feed molar flow rate [5]. Indeed, by using smaller catalysts in spherical reactors, the diffusional limitations of large catalysts, reducing the production rate can be eliminated [25].

One of the most serious computational challenges is to functionalize catalyst deactivation phenomena to engage it in the modeling procedure. Indeed, the catalyst deactivation mechanism and its empirical complexity should be rationalized in an applicable way. Amongst different deactivation models, the most suitable ones are those which closely fit the industrial data. With this background, catalyst deactivation have been involved and discussed in the dynamic models of methanol synthesis [26], naphtha reforming [27] and aromatic enhancement [28] processes in spherical packed bed reactors.

Particularly, Sadeghi et al. [29] proposed a mathematical model for a spherical catalytic reactor in which the long term catalyst deactivation was considered. They studied the catalyst deactivation and reactor performance as a function of different parameters in the reactor and reaction.

Investigation of the catalyst deactivation behavior have demonstrated that a number of parameters such as temperature, reactor size, carbon fuels and feed flow rates are very effective in the catalyst activity. In other words, the catalyst activity usually reduces with an increase in pellet radius, feed temperature, and flow rate. As a result, to find the optimum reactor productivity, the catalyst activity should be considered [30-33].

Generally, the pressure drop increases as the catalyst size decreases [34, 35]. The recently proposed Spherical Packed Bed Reactor (SPBR) configuration provides a promising solution to the hydrodynamic issues through a packed bed. SPBRs offer a higher cross sectional area in comparison with conventional tubular reactors; and thus, inherently have a lower pressure drop, which is the potential source of the mentioned difficulties in design, construction and operation of conventional reactors.

To date, two different types of continuous packed bed spherical reactors have been proposed: the radial-flow spherical reactors and axial-flow spherical reactors; each of which will be thoroughly describedand discussed in the following sections.

3-1- Radial-flow spherical reactor

Radial-flow spherical packed bed rectors (RF-SPBR), as the most known configuration of its kind, have been attracting attentions due to its wide applications and effective improvements in operating parameters. During the past years, various models have been developed, which have been become more and more reliable and meanwhile sophisticated. Thus, new conceptual approaches have been presenting to provide more accurate predictions of the reactor output.

A (continuous) radial-flow spherical reactor is constructed of two concentric spheres, and the catalysts fill the free space between them [36, 37]. The reactants radially flow from the outer surface through the inner one [36] or vice versa [38]. Indeed, the direction of flow was the center of attention in some previous publications [7, 39, 40]. They concluded that when an exothermic reaction took place in such reactors configuration the performance (yield and conversion) was affected by the flow direction. Subsequently, Vemuri Balakotaiah and Dan Luss [9] investigated the effect of flow regime (inward or outward) in isothermal reactions. They found out that the desired flow direction depends on the degree of reaction; i.e. for convex (which involves an increase in volume) and concave rate expressions (which involves a decrease in volume), the outward and inward flow direction was preferred, respectively. Moreover, they pointed out that generally the changes were not greatly significant and could be ignored in some cases.

Given the radial flow direction in spherical reactors, they possess a larger cross sectional area and smaller reactor thickness in comparison with traditional tubular reactors [41]. Consequently, the radial flow pattern leads to a significantly lower pressure drop. Besides, applying a spherical configuration for reverse flow reactors (RFR) causes a smaller reaction zone and higher temperature peak. Indeed, a spherical RFR has the potential for enhancing the flow rate and cycle duration (which is not plausible in a tubular reactor), causing a lower maximum temperature in these type of reactors [6, 38]. The structural characteristics of a radial flow spherical reactor are illustrated in Fig. 3.

Fig. 3

As mentioned, radial flow spherical reactor configuration has been applied to many processes, among which reforming of naphtha into hydrogen and aromatics has been received considerable attention. In this regard, Iranshahi et al. [36], studied the influence of major parameters, including

temperature and pressure on the hydrogen and aromatic production rates and the catalyst activity. Their results indicated that, the radial flow spherical reactor configuration resulted in a higher production rate in the naphtha reforming reactor and it overcame some drawbacks of the tubular reactor, such as the pressure drop. In addition, the temperature profile was lower along the proposed reactor, contributing to a reduction in catalyst deactivation rate. In another effort, the same authors tried to find the optimum operating conditions of the abovementioned reactor [42]. They found the maximum value of paraffins and naphthens consumption.

Because of the environmental concerns, diesel and fuel oils have been replacing with more sustainable gasoline and jet fuels; thus, hydrocracking process has been becoming a key sector of refineries. Recently, a radial flow spherical reactor have been suggested for hydrocracking process (HCP) [43]. RF-SPBR was considered as an alternative for the tubular catalytic reactor in the HCP and important parameters of the reactors, such as pressure drop, yield, and temperature profile were compared with the conventional reactor. Their results showed the slight value of pressure drop and increase of products yields in the spherical geometry in comparison with a tubular reactor, operating in the same conditions and catalyst load (Fig. 4). They investigated the simultaneous impact of feed flow rate and catalyst scale up on the spherical reactor yield. Moreover, an increase in the catalyst loading in the spherical configuration led to a more reactor productivity; on the other hand, the increase of the catalyst weight in the tubular reactor was not plausible and might damage the catalyst and reactor structure.

Fig. 4

Steam reforming of methanol is one of the principal routes for the production of hydrogen. Jiang et al. [44] investigated into mathematical analysis of different methanol steam reforming reactor schemes

for H_2 production. Their study proved that the most beneficial reactor was the spherical one, leading to minimum amount of required feed, and maximum reactor efficiency and productivity. Also, they concluded that by applying a Cu-based catalyst supported on Pt-Al_2O_3, the reactor could be designed to operate at room temperature.

Farsi et al. [5] simulated two and three-stage spherical radial flow reactors for DME production process. They proposed a steady-state heterogeneous model for methanol dehydration to DME. Their study showed an improvement about 2.83% and 3.15% for two and three-stage spherical reactors, respectively.

In 1993, Hartig and Keil [45] carried out a research to compare pseudo-homogeneous and heterogeneous modeling of a cascade of three large scale RF-SPBRs. Their study revealed that application of spherical reactors improved the production capacity and as a result the profit. In fact, under the same conditions, a spherical reactor with diameter of 6 m performs equally to seven tubular reactors. As can be seen, using a spherical reactor is considerably more cost-effective.

The periodic reversal of a feed flow direction (between inward and outward paths) through a continuous RF-SPBR traps a high temperature zone in the reacting area. Usually, this class of reactors is called reverse flow reactors. Viecco et al. [38], studied the operational properties of these reactors, applying a mathematical dynamic model developed under steady state condition for periodic fast switching of the flow direction. These researchers considered a spherical geometry shown schematically in Fig. 3. According to their results, despite lower temperature and concentration of the feed leading to an increase in the reaction rate, the hot spot at the center of the bed was smaller. Besides, the cooling zone in the downstream of the RFR causes a higher conversion (in comparison with a conventional adiabatic reactor) for reversible exothermic reactions. They also found that, the

required volume of the spherical RFR to achieve the desired conversion was lower than that of the tubular RFR.

3-2- Axial-flow spherical reactor

Radial-flow spherical reactors present a number of challenges like obtaining a uniform feed distribution and difficulty in using membranes [13]. These shortcomings are remedied in axial-flow spherical packed bed reactors (AF-SPBR). In this type of reactor, a fixed catalytic bed is placed between the two perforated screens as demonstrated in Fig. 5 [46]. Feed enters the top of the reactor and flows axially towards the bottom of the reactor. Indeed, the axial flow direction leads to a uniform flow distribution [28, 47]. In most of the studies regarding mathematical modeling and simulation of axial flow spherical reactors, axial flow pattern is considered to be dominant (radial flow is neglected) [46, 48, 49]. A significant hurdle to commercialization of axial flow reactors is to provide a uniform feed distribution in a way to avoid a two-dimensional flow regime. Hence, it is necessary to use flow distributors along the reactor axis [28].

As it can be conveyed from Fig. 5, the inlet and outlet cross-sectional areas are smaller than the cross-sectional area at the center of the reactor; thus, the existence of catalysts in these parts may cause considerable pressure drop and as a result, reduces the reactor efficiency [46]. Therefore, two screens are placed in the upper and lower parts of the reactor to hold the catalyst [28, 47]. Actually, apart from their application for controlling the pressure drop, these perforated screens are considered as mechanical supports and provide a better distribution of the flow [46].

Fig. 5

The axial flow spherical reactors have been theoretically investigated for many different processes, such as hydrocarbons reforming [46, 50], dehydrogenation of paraffins into olefins [24] and gasoline production [51]. The AF-SPBR superiority to the conventional tubular ones has been proved. Like other spherical reactors configurations, a number of important improvements obtained; such as lower pressure drop, higher production rate, suitable flow distribution, and desirable temperature profile. More importantly, a membrane reactor can have an axial flow spherical structure; and consequently, enjoys the advantages of both membrane and spherical reactors.

In a membrane reactor, the desired products are removed from the reaction media, and based on the Le Chatelier's principle [52, 53], the chemical equilibrium shifts towards the products side [54]. Moreover, by removing the products, the residence time in the reactor increases and so does the conversion. A characteristic feature of membrane reactor is the fact that the reaction and separation take place at the same time. As a result, this beneficial reactor configuration reduces the cost of upstream separation unites. In fact, the selective removal of products of a reaction not only offers higher yields, but also improves selectivity for the product of interest [55].

Incorporation of membranes in the internal design of a RF-SPBR has encountered difficulties. In contrast, it is plausible to manufacture a membrane assisted axial-flow spherical reactor [28], named as MAF-SPBR. The main difference between the membrane and the non-membrane configurations is that, in the first one, the inner sphere is coated by an appropriate perm-selective membrane layer. Thus, the reaction shifts toward the production side, and an improvement in product yields can be achieved. Fig. 6 shows the schematic design of a membrane axial flow spherical reactor. Studies showed that, the special geometrical design of a spherical reactor provides the potential of significant reduction in the total surface area of the membrane (about 80%) compared with the conventional

membrane TRs [16]. This is followed by a great reduction in capital costs of construction and maintenance expenses of the operation [28].

Fig. 6

In 2011, Rahimpour et al. investigated the applicability and efficiency of utilizing membrane technology in a spherical naphtha reforming reactor [28]. Their proposed reactor configuration was an axial flow spherical membrane reactor, in which the inner wall of the sphere assumed to be coated with a composite perm-selective membrane; a thin Pd-Ag layer. As anticipated, the effective role of this configuration in the enrichment of aromatics yields as the main product, as well as the enhancement of hydrogen purity and quality as a precious side product was confirmed. Afterwards, the same research team [25] proposed the same reactor configuration for methanol synthesis process. Their study not only proved the superiority of the MAF-SPBR rather than the conventional TR and RF-SPBR configuration, but also emphasized the remarkable role of a spherical geometry in resolving pressure drop and consequent difficulties in the reactor. Subsequently, in 2013, Samimi et al. investigated this configuration for dimethyl ether (DME) synthesis by methanol dehydration [56]. This configuration resulted in 13.5% increase in DME mole fraction, as well as approximately 98% reduction in pressure drop along the packed bed. Fig. 7(a) compares the DME mole fraction in TR, MAF-SPBR and optimized MAF-SPBR, and Fig. 7(b) presents a comparison of pressure profiles between a conventional TR and AF-SPBR.

Fig. 7

As mentioned, a membrane assisted reactor brings about many benefits; on the other hand it suffers from some shortcomings, which should be considered in designing of such a reactor. For instance,

using a hydrogen perm-selective membrane in naphtha reforming process leads to the rapid reduction of H_2/HC ratio, which is a very important factor in catalyst deactivation. Hence, its level must be controlled to be higher than a specific value (usually 4) [57]. This implies that owing to the novelty of the idea, taking advantages from the membrane technology in a spherical reactor for various processes have been faced some difficulties and still seeks more analytical investigations.

3-3- Multi-reactor setup systems

According to the purpose of a process, combinations of different reactor structures have the potential to improve the overall performance. For example, suitable arrangements of tubular and spherical reactors leads to improvement of production capacity [58]. Various mathematical models have been successfully developed to predict the performance of such reactor set-ups. Farsi et al. [59] investigated the possibility of improving the production capacity of DME production by increasing the number of reactors. Fig. 8 illustrates the process flow diagram for DME production in a conventional tubular reactor and the proposed three stage spherical structure. As can be observed in Fig. 9, higher DME production rate is achieved for a large scale spherical reactor arrangement, while for a TR this is not feasible owing to the pressure drop limitations.

Fig. 8

Fig. 9

Rahimpour et al. investigated different combinations of spherical radial flow and membrane axial flow tubular reactors for naphtha reforming process [58]. They suggested a homogeneous, one-dimensional reactor model, in which three different configurations of SST, STS, and TSS (T and S represents the membrane tubular and non-membrane spherical reactor respectively), were discussed.

The schematic diagram of the three possible configurations is presented in Fig. 10(a-c). In their study, not only a higher hydrogen and aromatics production were obtained, but also the pressure drop considerably reduced in all the proposed configurations. It is noteworthy to mention that the spherical reactor requires lower membrane area. Fig. 11 clearly shows the difference between the pressure drop in tubular and spherical reactors.

Fig. 10

Fig. 11

In a similar work, Iranshahi et al. [16], compared 8 different arrangements of radial flow spherical and membrane tubular naphtha reforming reactors to find the most desired combination (the one results in the maximum yield of major products). In other words, they considered all the possible set up systems of three serial reactors, using membrane tubular reactor (T) and non-membrane spherical reactor (S), as: TTT, SSS, TST, TSS, STT, STS, SST, TTS. Their results demonstrated that the STS and STT combinations had the best performances among all the other combinations. These configurations took the advantage of lower pressure drop of spherical reactor, and at the same time the higher conversion of tubular membrane reactor. Furthermore, in this study, the performances of the two best combinations (STS and STT) were optimized, named as OSTT and OSTS. The last was suggested as the best set up of spherical and membrane tubular reactors for naphtha reforming process. Fig. 12(a-c) depicts the considerable augmentation in the hydrogen and aromatic production rates in these reactor set ups. Fig. 12(d) sows the difference between the pressure drop in the two optimized reactor configurations and the conventional tubular reactor, proving the lower pressure drop in the proposed configurations.

Fig. 12

Further studies on the performance of multi-reactor systems for DME [5, 60], methanol [26] and styrene [61] synthesis have also indicated that increasing the number of stages of spherical and/or membrane tubular reactors would lead to an increase in the quality and capacity of production. A summary of different spherical reactors applied in different processes is provided in table 1.

Table 1

3-4- Modeling and optimization of packed bed spherical reactors

A reliable mathematical model, which can predict the operability of a chemical reactor, is based on the thermodynamic, kinetic, heat and mass transfer correlations, as well as fluid flow patterns [62]. To this end, multiple computational modeling and simulations have been employed for the spherical reactors. The dynamic models are regularly composed of heat and mass conservation equations coupled with a number of thermodynamic, kinetic, and a set of empirical correlations for predicting physical properties. Several essential assumptions have been applied in each work, for the sake of simplification. In most of the studies, for packed bed reactors, a one-dimensional plug flow model has been developed; and for unpacked reactors, lumped system has been considered. Homogeneous, pseudo-homogeneous, or heterogeneous reactor phases have been considered in models, depending on the system characteristics [25, 42, 63]. Orthogonal collocation method has been frequently employed as a reliable numerical approach for solving the modeling equations [43, 49]. Finally, the simulation results have been compared with actual data to validate the accuracy of the proposed models.

Optimization also plays an important role in chemical engineering, especially when trying to gain the best results with a least consumed resources and additional undesirable products. Using

mathematical models for reactors, the velocity, temperature and concentration profiles are simultaneously taken into account in order to find optimal operating conditions. For a spherical reactor, many different decision variables have been considered such as inlet temperatures, concentration profile, temperature along the reactor, reactor radius [64], length per radius [56], total pressure of the process, catalyst distribution in reactors [42], and number, combination and arrangement of stages [37, 45]. The main aim of an optimization study is to find the operating conditions, contributing to maximum reactants conversion and molar flow rate of the major products. In almost all the cases, these optimum conditions can be ultimately influenced by the factor of profit and HSE [5, 16, 65, 66].

The most recent, popular and practical optimization techniques that have been employed on chemical reactors are: Simulated Annealing (SA) [67], Evolution Strategies (ES) [68], Genetic Algorithm (GA) [69, 70], Differential Evolution (DE) [71] and iterative dynamic programming (IDP) [45]. These methods have been frequently applied in the recent studies, due to their speed and good convergence, in comparison with the traditional techniques. Quantitatively, differential evolution have been the most common optimization method for spherical reactors [5].

DE is a population based algorithm similar to genetic algorithms with similar operators: crossover, mutation, and selection. The major difference is that genetic algorithms rely on crossover, while DE depends on mutation operation in order to construct more reliable solutions. This optimization procedure is based on the differences of randomly selected pairs of solutions in the population. The algorithm uses mutation as a searching mechanism and selection operation to guide the search toward the possible regions in the search space. Moreover, the DE algorithm uses a non-uniform crossover that can choose parameters of child vector from one parent more than it takes from the others. By

means of the components from the existing population members for creating trial vectors, the crossover operator efficiently shuffles information around successful combinations; and thus, it results in higher probability of solution space [72-74].

DE has been considered as the optimization technique for the spherical reactors of many different processes, such as methanol production [17], naphtha reforming [16, 57], dimethyl ether (DME) synthesis [75]. Iranshahi et al. [16] applied this algorithm and optimized eight possible combinations of tubular and spherical reactors. The details of their results are demonstrated in section 3.3, (multi-reactor setup systems). Samimi et al. [59] applied DE algorithm to maximize the DME production rate. Their proposed reactor design led to an increase of 16.3% in DME production rate and a decrease in reactor diameter and thickness. Farsi et al. [61] optimized multi-stage spherical reactors of ethylbenzene dehydrogenation to styrene. They considered a multi-objective optimization problem, aiming to find the desired inlet temperature, resulting in optimum styrene production rate; and meanwhile, the minimum of toluene and benzene production rates. Table 2 provides a comparison between different optimization procedures; i.e. objective functions, decision variables, and constraints; applied for spherical reactors.

Table 2

3-5- Catalyst challenges in packed bed spherical reactors

From an engineering viewpoint, small catalyst pallets are not applicable, since they cause a considerable pressure drop in packed beds. Therefore, internal diffusion rate inside catalyst particles, and in commercial scale, mass and heat transfer limitations inside the reactor must be considered in design [16, 24]. With the favor of reduced pressure drop, the spherical reactor takes advantage of

operating with preferably smaller catalyst pellets, higher catalyst effectiveness factor and feed molar flow [5]. As a result, the diffusional limitations of larger catalyst particles, which hinders the production rate can be eliminated [25].

From a computational standpoint, the mechanisms of catalyst deactivation and method of engaging theoretical and/or empirical sourced deactivation functions in the simulations have been a serious challenge for researchers, especially in the field of petroleum industry. As mentioned, a useful deactivation model should have the potential to predict industrial data with a low error. With this background, catalyst deactivation have been involved and discussed in the dynamic models of methanol synthesis [26], naphtha reforming [27] and aromatic enhancement [28] processes in the spherical packed bed reactors.

Sadeghi et al. [29] proposed a mathematical model of a spherical catalytic reactor in which the long term catalyst deactivation was incorporated.

Their model focused on the effects of the reaction and reactor parameters on the catalyst deactivation and performance of the reactor. They verified the catalyst deactivation and reactor performance as a function of reaction and reactor parameters.

3-6- Comparison of tubular and spherical packed beds

The comparison of conventional tubular and spherical reactors reveals that the latter possesses many desirable characteristics. In a novel spherical reactor we can claim that:

- The pressure drop significantly decreases.
- The safety and maintenance of the plant highly increases.

- The reactor body has a lower thickness.
- The required surface area of the membrane decreases, resulting in an effective reduction of the investment costs during the operation.
- Smaller catalyst pellets can be applied with higher effectiveness factor and overcome mass transfer limitations.
- More significant molar flow rate can be used, contributing to higher production rate.
- Larger reactor scales; and thus higher capacity of plant would be available.
- Lower power supply for recompression is required.

In addition, the AF-SPBR is commonly preferred to the RF-SPBR since:

- The axial flow pattern is more easily applicable in spherical reactors [46].
- AF-SPBR is flexible in applying modifications for more effective contact between the reactant phase and the catalytic bed [51].
- Membrane technology can be easily used in the AF-SPBR, while it is difficult to apply on RF-SPBR [46].

4- Unpacked spherical vessels

Unpacked Spherical tanks are commonly applied for liquid phase reactions in many processes [76, 77]. It has been proved that a spherical vessel is remarkably practical for stirred reactors; as their motionless zones are negligible [78]. A perfectly-mixed reactor serves as a practical tool for investigating the reaction mechanism, because perfect mixing can usually occur at small scale [79].

Tyler [80] and Ashmore et al. [81] proved that in the case of a gas phase spherical reactor, natural convection term is considerable when Rayleigh number is above ~600. Jones [82] noted that due to the fact that temperature gradient is perpendicular to the gravity force, there exist always some convection inside a cylinder or a sphere. Indeed, the effect of natural convection is considerable on exothermic reactions; in which the released heat by an exothermic reaction causes a temperature gradient inside a reactor; and consequently, a natural convection stream occurs in the reactor [83].

In this context, study of the unpacked reaction tanks (of whether mixing/non-mixing types) have been the case study of some researchers. Table 3, presents a summary of previous publications, investigating unpacked spherical reactors.

Table 3

5- Guidelines for further development

Although several authors have studied various aspects of spherical reactors and a number of papers have been published in this area, more researches are needed to characterize the performance and improvement of the yield of reactions with this configuration. As a guideline for further investigations, the following suggestions are proposed:

1. Spherical reactor configuration can be applied for other processes with a conventional tubular reactor; and the simulation results can be compared with the conventional data to assure the benefits of spherical reactors.
2. More investigations concerning environmental aspects, commercial viability and economic feasibility of the proposed configurations are necessary.

3. Results of optimizing analysis on spherical reactor have clearly indicated that, using preferably more complicated models rather than conventional simple models lead to more reliable results. To this end, the number of assumptions, on which the mathematical models are derived, should be reduced. For instance:

- Considering various catalyst distribution or different hot-spot temperatures in the model.
- In most of the previous publications, a one-dimensional model has been assumed (only in axial or radial direction) while considering the two-dimensional model definitely provide more accurate results. Also, a comparison between one and two-dimensional mathematical modeling to specify the most accurate and optimum assumptions in terms of accuracy and computational cost would be very interesting. It is worth mentioning that, all of the previous studies have used Cartesian coordinate, and there is not any study, using the spherical coordinate system.
- Presented reactor models commonly assumed a homogeneous fluid flow. Considering heterogeneous reacting flow inside the reactor is suggested for improvement of the simulation results.

4. Given the fact that most studies, regarding spherical reactors deal with the theoretical investigations, there is a considerable need for experimental researches. Comparisons between simulation results and plant data should be considered in order to determine the degree of conformity of theoretical investigations.

5. The application of membrane in the RF-SPBR need more experiments. Manufacturing an applicable and bearable spherical shape membrane or modification of details in design of the reactor are some of the examples.

6. Designing a spherical reactor, its cost evaluation, and its scaling up to industrial production plants should be considered from different perspective.

6- Conclusion

In any process, there is a significant incentive to minimize pressure drop in reaction vessels and this has led to the development of several reactor configurations alternatives. Choosing a spherical geometry for industrial reactors has appeared as a highly interesting idea, which imposes preferably lower pressure drop through the catalytic bed, and investment cost.

This review article provided comprehensive information regarding various aspects of spherical reactors. Indeed, modeling, simulation, optimization, design and experimental studies regarding this reactor configuration were reviewed. Two main groups of spherical reactors namely radial and axial-flow-spherical-catalytic-reactors were presented and discussed.

Afterwards, comparisons between spherical and conventional tubular reactors as well as between radial and axial-flow spherical reactors were performed. The superiority of novel spherical configuration was proved and axial-flow spherical configurations were verified to be the most efficient and reasonable alternative for conventional reactors. As a general conclusion, this review proves that application of spherical reactors contributes to higher reaction rates, production capacity, and more energy efficient processes.

List of Figure:

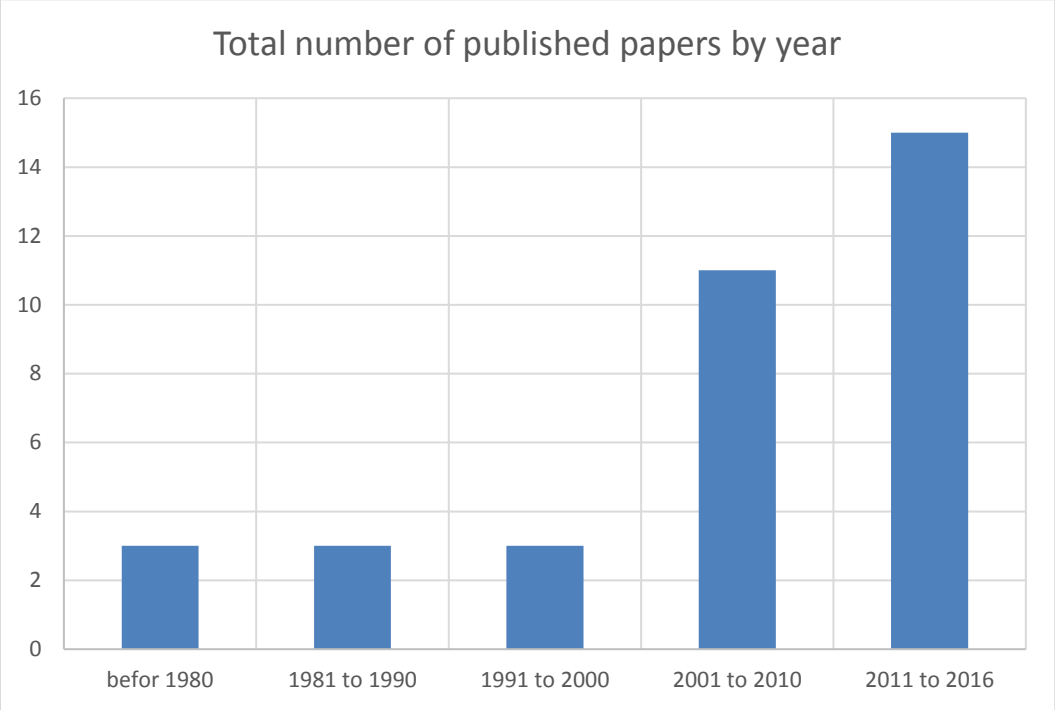

Fig. 1: The trend of total number of published papers by year

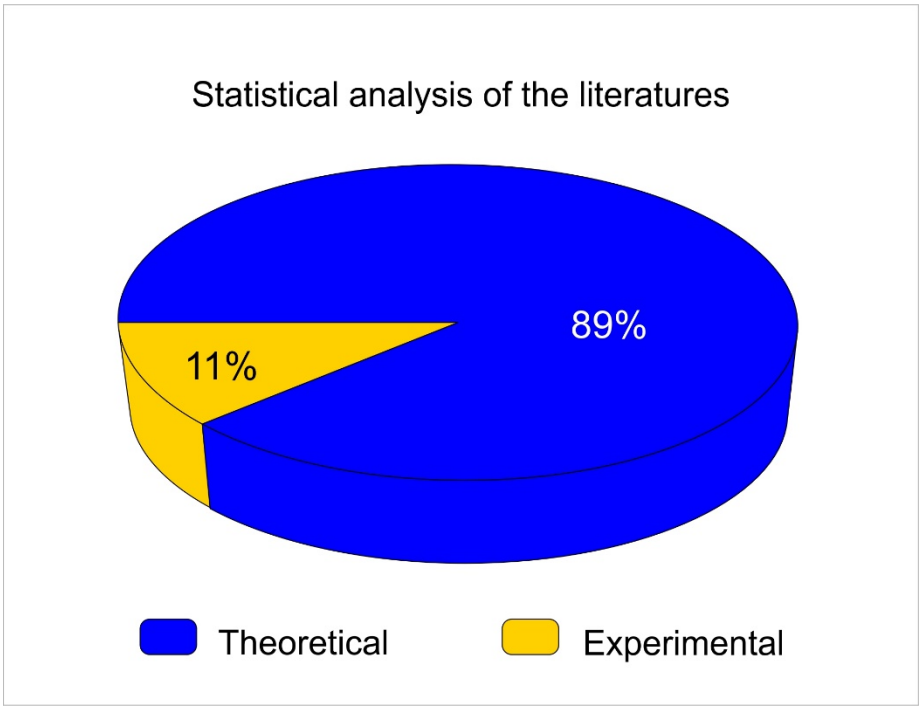

Fig. 2: The percentage of theoretical and experimental efforts on spherical reactor

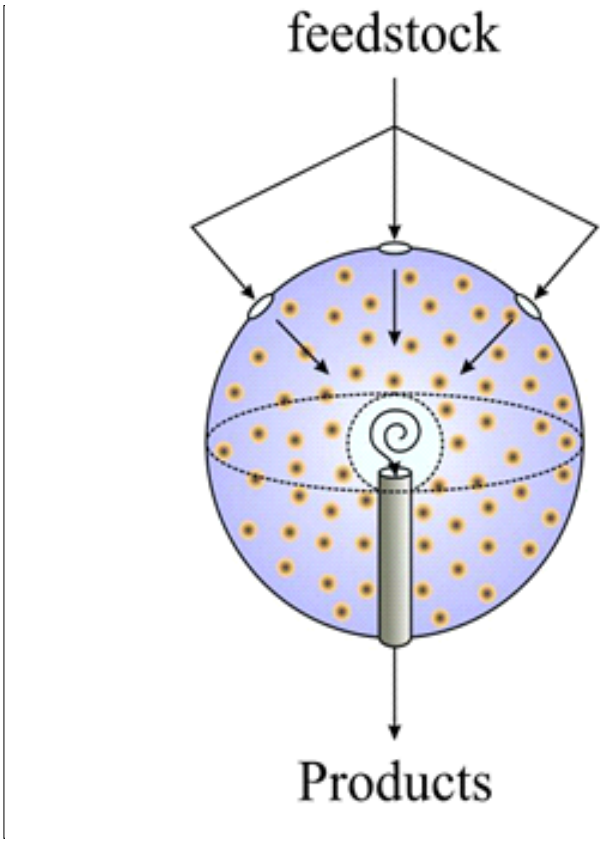

Fig. 3: Schematic of a radial flow spherical reactor

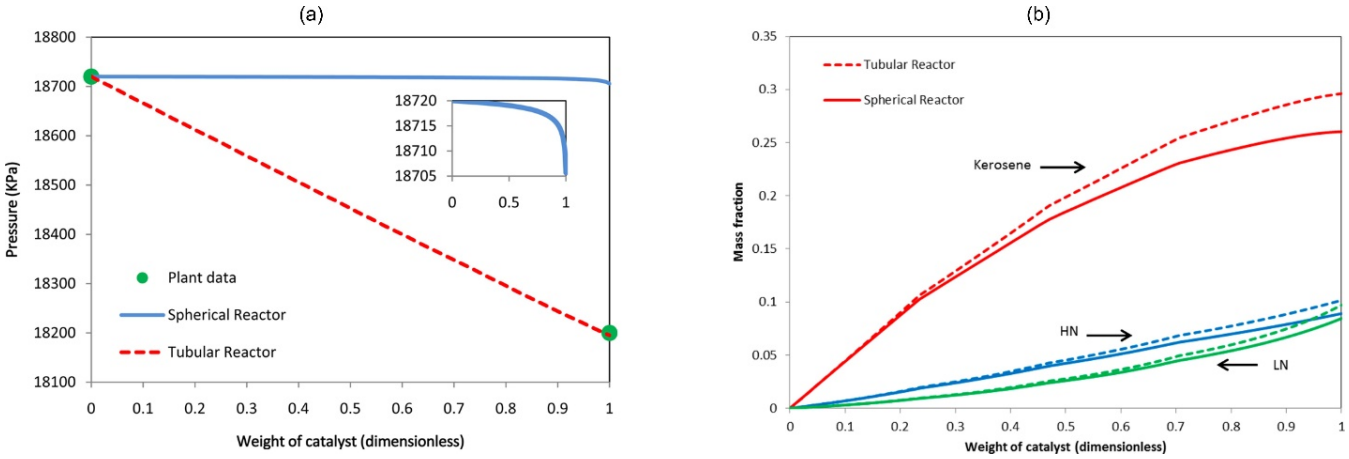

Fig. 4: (a) Comparison between pressure profiles in the tubular reactor and the spherical reactor in the hydrocracking process, (b) Comparison between products yields of kerosene, light naphtha and heavy naphtha in the tubular reactor and the spherical reactor in the hydrocracking process

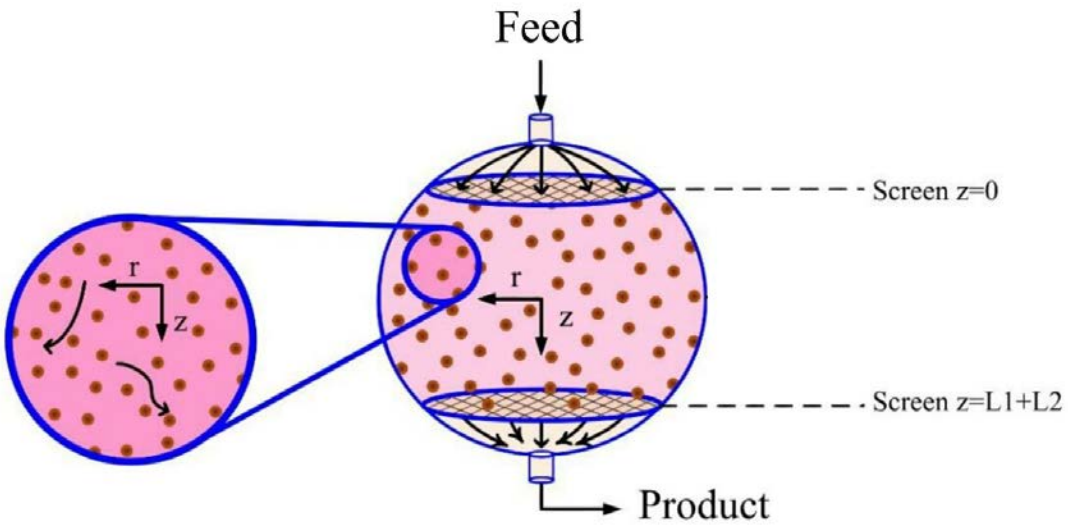

Fig. 5: Schematic of an axial flow spherical reactor

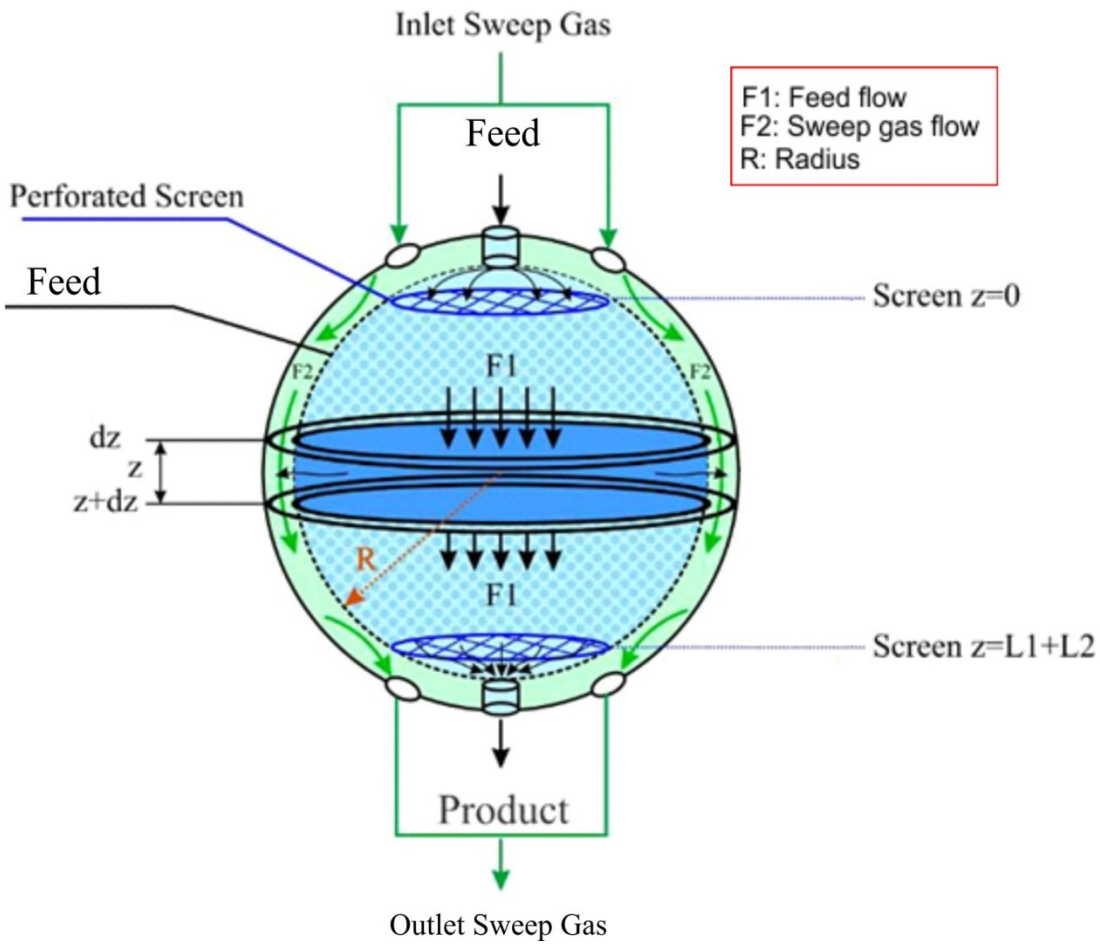

Fig. 6: Schematic design of a membrane axial flow spherical reactor

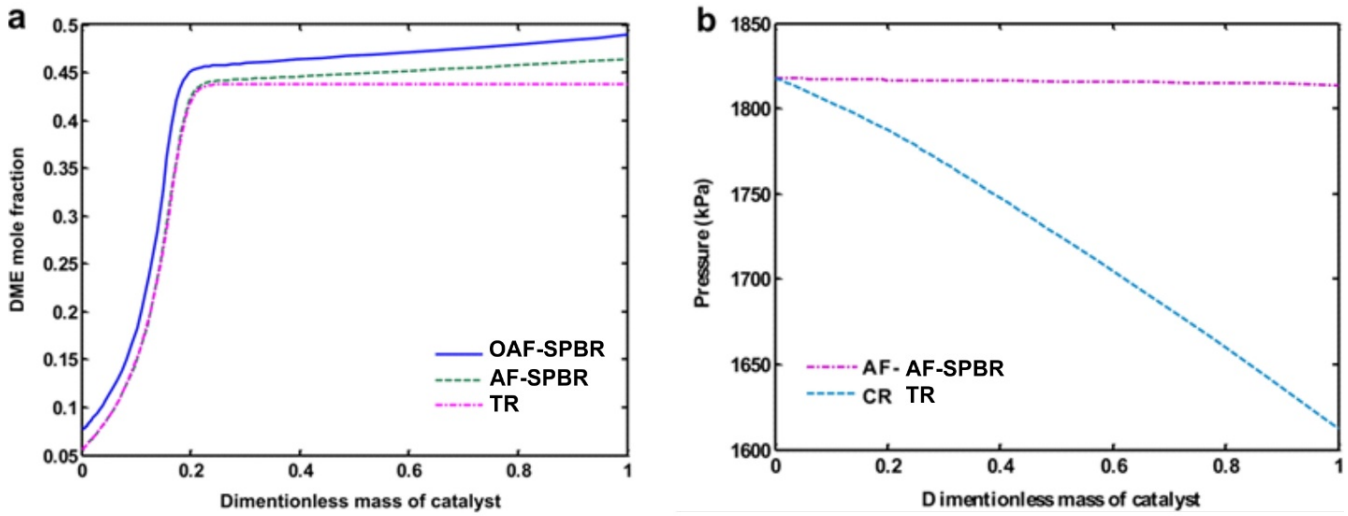

Fig. 7: (a) Pressure profile of the spherical and conventional reactor for DME production, (b) DME mole fraction

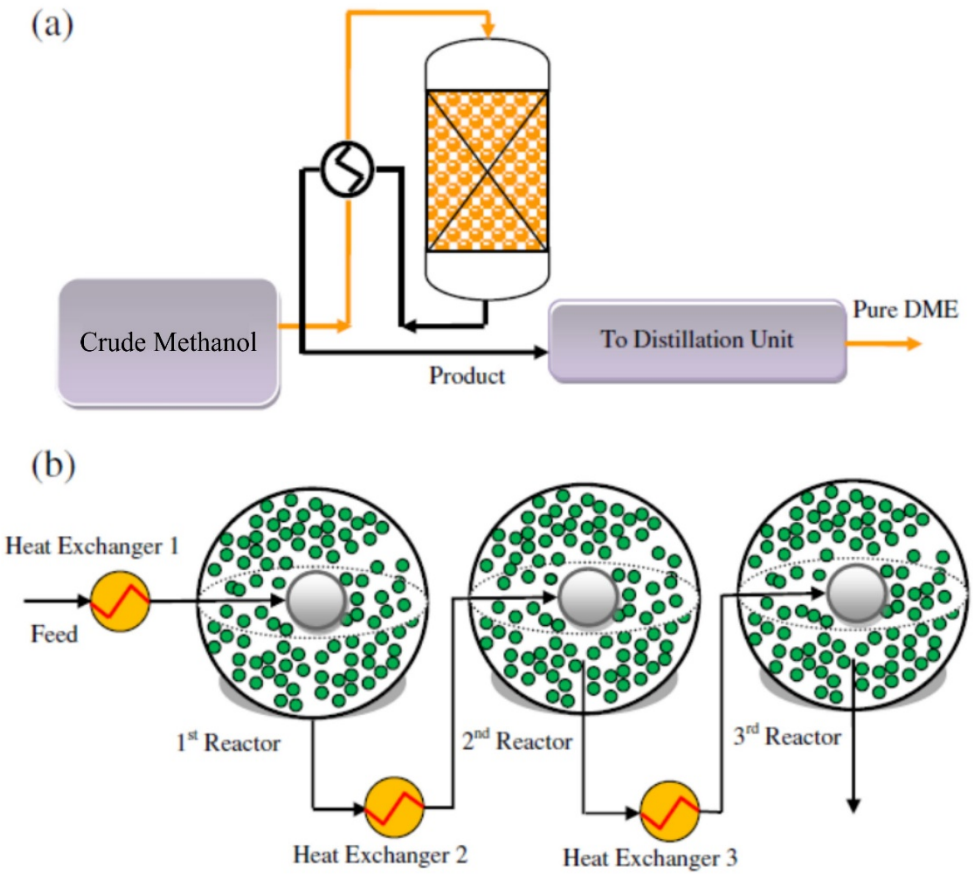

Fig. 8: (a) Process flow diagram of DME production in a fixed bed reactor, (b) Three-stage spherical configuration

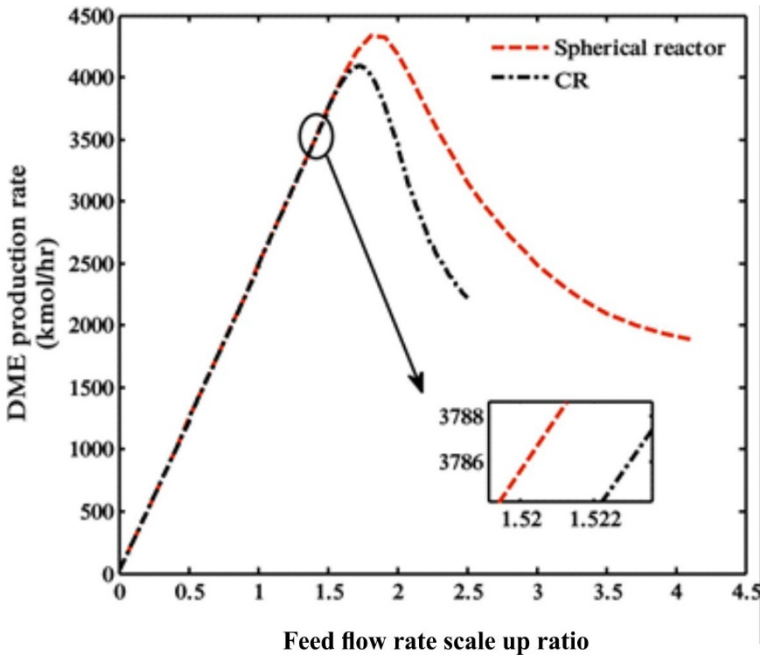

Fig. 9: A comparison between a single spherical reactor in series and a conventional type on DME production rate versus feed flow rate scale up ratio

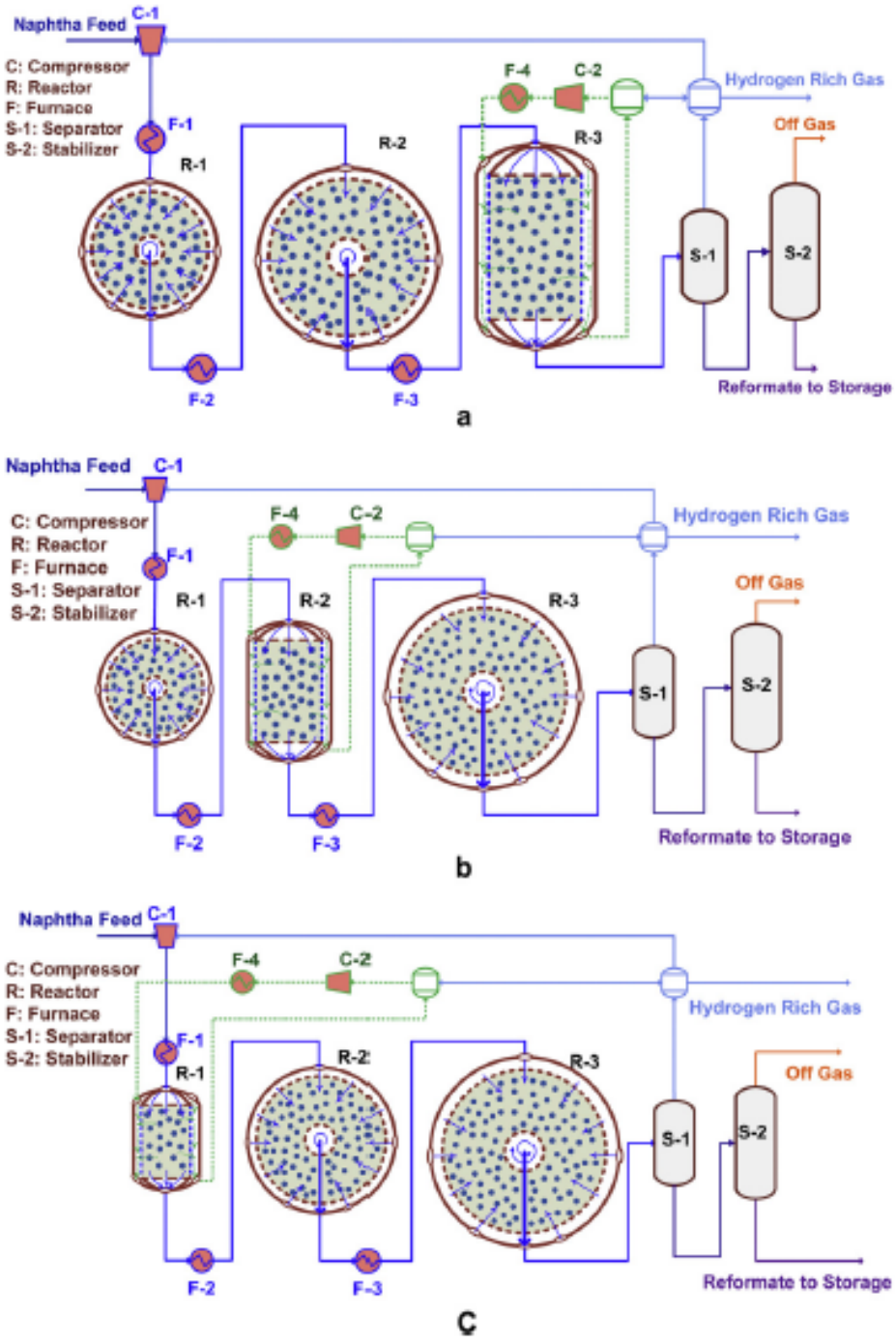

Fig. 10: Schematic diagram for (a) SST, (b) STS and (c) TSS configurations

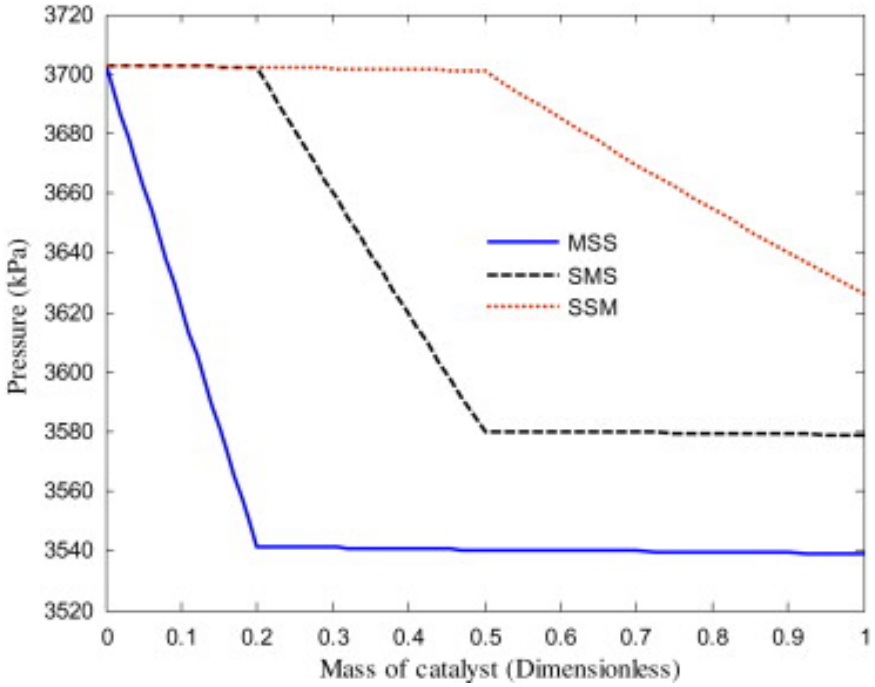

Fig. 11: Pressure drop through the reactor for SST, STS and TSS configurations

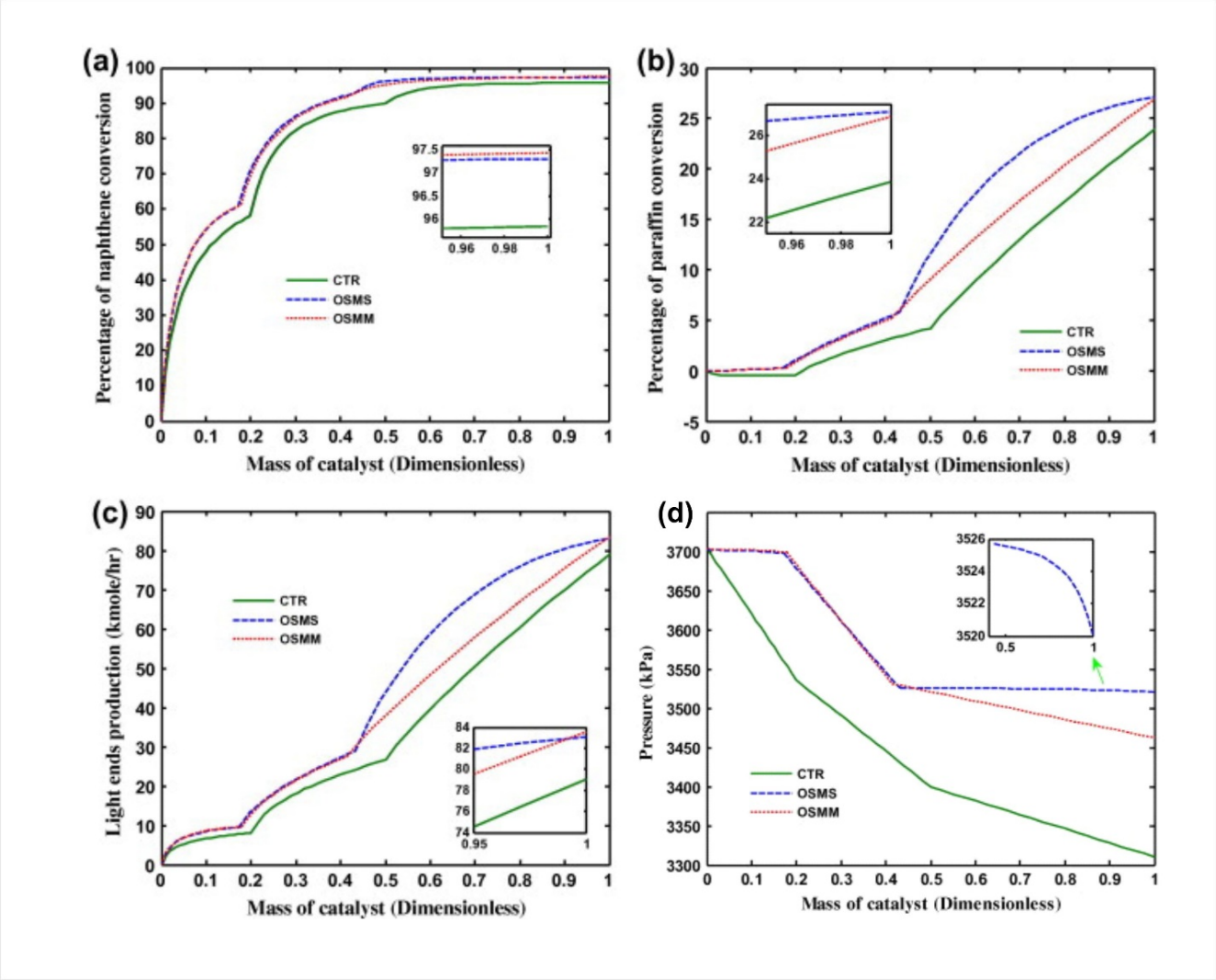

Fig. 12: (a) The percentages of naphthene conversion, (b) The percentages of paraffin conversion, (c) Light ends production rate along single tubular reactor, OSMS and OSMM, (d) Pressure profile along single tubular reactor, OSMS and OSMM

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Table 1. A summary of reported spherical reactor designs for various processes

System	Flow regime	Number of reactors in the process	Temperature (K)	Pressure (bar)*	Catalyst	Membrane	Optimization
Methanol synthesis	Radial	3	510-550	~81	$Cu/ZnO/A1_2O_3$	-	IDP
Naphtha reforming	Radial	3	720-780	33-37	$Pt/Re/Al_2O_3$	-	-
Naphtha reforming	Axial	3	720-780	33-37	$Pt/Re/Al_2O_3$	-	-
Naphtha reforming	Radial	3	720-780	33-37	$Pt/Re/Al_2O_3$	-	DE
Methanol synthesis	Radial	3	470-520	~77	Cu/ZnO	-	DE
Naphtha reforming	Axial	3	720-780	33-37	$Pt/Re/Al_2O_3$	Pd-Ag membrane for separation of H_2 from reaction media	-
Methanol synthesis	Radial	Comparison of single, dual, and three stage reactor set up were considered.	500-530	~77	Cu/ZnO	-	-
Methanol synthesis	Axial	Comparison of single, dual, three, and four stages reactor set up were performed.	500-530	74-77	Cu/ZnO	-	-
Naphtha reforming	Radial	3	720-780	33-37	$Pt/Re/Al_2O_3$	Pd-Ag membrane for separation of H_2 from reaction media	-
DME synthesis	Axial	2	500-660	16-18.2	γ-Al_2O_3	-	DE
DME synthesis	Axial	1	500-660	16-18.2	γ-Al_2O_3	Alumina–Silica composite membranes	DE

						for water separation	
Naphtha reforming	Radial	3	720-780	33-37	$Pt/Re/Al_2O_3$	Pd-Ag membrane for separation of H_2 from reaction media	DE
DME synthesis	Radial	3	520-660	16-18.2	γ-Al2O3	-	-
Naphtha reforming	Axial	3	720-780	33-37	$Pt/Re/Al_2O_3$	Pd-Ag membrane for separation of H_2 from reaction media	DE
Naphtha reforming	Axial	3	720-780	33-37	$Pt/Re/Al_2O_3$	-	DE
Naphtha reforming**	Axial	3	720-780	33-37	$Pt/Re/Al_2O_3$	-	-
DME production	Radial	Single and dual stage membrane reactors were compared.	520-660	16-18.2	γ-Al_2O_3	Alumina–Silica composite membranes for water separation	-
styrene production	Radial	3	820-910	1.06-1.26	Potassium-promoted iron oxide	-	Genetic algorithm (Multi-objective)
Hydrocracking	Radial	1	640-700	182-187	Bi-functional (having metallic and acidic sites)	-	-

*The changes in pressure are related to conventional (tubular) systems.
**1D and 2D models are compared.

Table 2. A summary of optimization problems applied for spherical reactors

System	Optimization algorithm	Objective function	Decision variables	Constraint
Methanol synthesis	IDP*	Catalyst volume was minimized.	• Inlet temperature • Diameters of the inner spheres	• $T^{cat} \leq 553K$ deactivation) • The outer dia reactors are e production o spheres is mu
Naphtha reforming	DE/best/1/bin	$\frac{Y_{H_2}^{Out}}{Y_{H_2}^{In}} + \frac{Y_{Aromatic}^{Out}}{Y_{Aromatic}^{In}}$ was maximized.	• Inlet temperature of the first, second, and third reactor • Total pressure • Catalyst distribution in the first, second, and third reactor	• $(\frac{H_2}{HC})_i \geq 4.71$ deactivation) • $\sum_{i=1}^{3} W_i = 1$ (th catalyst weig equal to unit
Naphtha reforming	Basic DE	$H_{31} = (F_{H_2}^{Out} - F_{Aromatic}^{Out})$ $H_{32} = (\frac{F_{Aromatic}^{Out} - F_{Aromatic}^{In}}{F_{Naphtha}^{In}}) + (\frac{F_{H_2}^{Out} - F_{H_2}^{In}}{F_{Naphtha}^{In}})$ $H_{33} = (F_{Paraffin}^{Out} + F_{Naphthane}^{Out} + F_{Aromatic}^{Out})$ $H_{34} = (\frac{F_{Aromatic}^{Out}}{F_{Paraffin}^{Out} + F_{Naphthane}^{Out} + F_{Aromatic}^{Out}})$ $(H_{31} + H_{32} + H_{33} + H_{34})$ was maximaized.	• Length to diameter ratio for tubular membrane reactors • Naphtha feed pressure to the first reactor • Sweeping gas pressure in tubular membrane reactor • Hydraulic diameter for the tubular membrane reactor • Sweeping gas molar flow rate • Membrane thickness • Catalyst mass distribution in the first, second, and third reactor • Inner radius of the spherical reactors • Hydrogen mole fraction in recycled stream • Fresh naphtha feed molar flow rate • Hydrogen mole fraction in sweeping gas • Naphtha inlet temperature • Sweep gas inlet temperature	$(\frac{H_2}{HC})_i \geq 4.73$ $\sum_{i=1}^{3} W_i = 1$ $P_1^{In} - P_3^{Out} \langle 373$ pressure drop i is lower than th tubular reactor
Naphtha reforming	Basic DE	$Y_{H_2} + R_{ref} + x_{Aromatics}$ was maximaized.	• Length to diameter ratio • Catalyst mass distribution for the first, second, and third reactors • Fraction of total sweep • Membrane thickness • Sweep gas pressure • Total molar flow rate of sweep gas • Hydraulic diameter for the first, second, and third reactors • Hydrogen mole fraction in the recycled stream • Hydrogen mole fraction in the sweeping gas • Total fresh naphtha feed to the first reactor • Compressor discharge pressure to the first reactor	$(\frac{H_2}{HC})_i \geq 4.73$ $\sum_{i=1}^{3} W_i = 1$ $\sum_{i=1}^{3} N_i = 1$ (the fraction of swe reactor should $P_1^{In} - P_3^{Out} \langle 100$

Naphtha reforming	Basic DE	$\frac{Y_{H_2}^{Out}}{Y_{H_2}^{In}} + \frac{Y_{Aromatic}^{Out}}{Y_{Aromatic}^{In}}$ was maximaized.	• Catalyst weight distribution for the first, second, and third reactors • Inlet pressure • Length to diameter ratio • Naphtha feed molar flow rate • Hydrogen mole fraction in the recycle stream • Inlet temperat1ure of the first, second, and third reactors	$(\frac{H_2}{HC})_i \geq 4.74$ $\sum_{i=1}^{3} W_i = 1$
Methanol synthesis	Basic DE	x_{MeOH}^{Out} was maximaized.	• Inlet temperatures • Temperatures profiles • Reactor radius ratio	-
DME synthesis	Basic DE	F_{DME}^{Out} was maximaized.	• Inlet temperature • Catalyst distribution for each reactor	$\sum_{i=1}^{2} W_i = 1$ $495 \leq T \leq 650K$
DME synthesis	Basic DE	Y_{DME}^{Out} was maximaized.	• Reactor inlet temperature • Permeation side inlet temperature • Reactor inlet molar flow rate • Permeation sides inlet molar flow rate • Feed composition • Initial composition of permeation side • Reactor inlet pressure • Length to radius ratio	$495 \leq T \leq 650K$
Styrene production	Genetic algorithm	*Single objective:* $f(x) = -\omega_1 x_{Styrene} + \omega_2 (x_{Toluene} + x_{Benzene})$ was minimized. *Multi- objective:* To simultaneously maximize styrene production, and minimize side reactions	• Feed temperature of the three reactors	$T_i \leq 700°C$ $i = 1,2,3$

*The (Iterative dynamic programming) IDP method was compared with sequential quadratic programming (SQP) and the Box complex method

Table 3. An overview of the investigations using unpacked spherical vessels.

No	Description of study	Analysis type	Researcher(s)
1	A batch unpacked spherical reactor was applied to investigate the effect of heat transfer by natural convection and diffusion mechanisms on the occurrence of Sal'nikov's chemical reaction.	Heat transfer and Thermal effects	Campbell AN et al.
2	The effect of natural and forced convection on thermal explosion in an unpacked spherical reactor was investigated.	Heat transfer and Thermal effects	Liu T et al.
3	The effects of natural convection and consumption of reactant during a thermal explosion inside an unpacked spherical reactor.	Heat transfer and Thermal effects	Liu T et al.
4	Heat and mass natural convection as well as diffusion in an unpacked spherical reactor was verified in which the explosive reaction of azomethane decomposition took place.	Heat transfer and Thermal effects	Gerri and Kaufman
5	A numerical model was developed for decomposition of the gas, azomethane, reaction between nitric oxide and oxygen, as well as between hydrogen and chlorine, occurring in a spherical reactor.	Heat transfer and Thermal effects	Tyler and Ashmore
6	The effects of the operating parameters of the spherical and tubular reactor on Fluid flow	Fluid dynamics	Blichner O
7	The effects of reactant consumption on thermal combustion in a spherical reactor with both natural and forced heat convection were considered.	Thermal combustion and heat effects	Azevedo et al.
8	Thermo-kinetic study of the oscillatory combustion of hydrogen in a spherical glass reactor was studied.	Kinetics and thermodynamics of combustion	Baulch et al.
9	Dynamics of combustion processes of n-heptane and i-octane with varying temperature and pressure were investigated.	Dynamics of thermal combustion	Lignola et al.
10	Based on maximum second derivative of pressure rise, an approach for determination of the flammable limits of gases was suggested.	Combustion	Crowl et al.
11	An unpacked spherical reactor was proposed for making suspension of solid particles.	Fluid dynamics	Taca et al.

Abbreviation	Definition
AF-SPBR	Axial-Flow Spherical Packed Bed Rector
Cat	Catalyst
DE	Differential Evolution
DME	Dimethyl Ether
ESs	Evolution Strategies
GAs	Genetic Algorithms
HC	Hydrocarbon
HSE	Health, Safety and Environment
I	Numerator of reactor
IDP	Iterative Dynamic Programming
In	Inlet condition
MAF-SPBR	Membrane Axial-Flow Spherical Packed Bed Rector
MeOH	Methanol
N	Fraction of sweep gas flow
OAF-SPBR	Optimized Axial-Flow Spherical Packed Bed Rector
Out	Outlet condition
P	Pressure
RF-SPBR	Radial-Flow Spherical Packed Bed Rector
SA	Simulated Annealing
SPBR	Spherical Packed Bed Rector
OSMS	Optimized spherical–tubular membrane-spherical
OSMM	Optimized spherical reactor and two subsequent tubular membrane reactors
SSS	Non-membrane Spherical- Non-membrane Spherical- Non-membrane Spherical
SST	Non-membrane Spherical-Non-membrane Spherical-Membrane Tubular
STS	Non-membrane Spherical -Membrane Tubular- Non-membrane Spherical
T	Temperature
TR	Tubular Reactor
TSS	Membrane Tubular- Non-membrane Spherical – Non-membrane Spherical
TTT	Membrane Tubular- Membrane Tubular- Membrane Tubular
W	Catalyst weight fraction
X	Mole fraction
Y	Yield
ω	Weights for objective function

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