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Review

A review of cleaner production methods for the manufacture of methanol

Amjad Riaz [a,b], Gholamreza Zahedi [c,*], Jiří Jaromír Klemeš [d]

[a] Process Systems Engineering Centre (PROSPECT), Department of Chemical Engineering, Faculty of Chemical Engineering, Universiti Teknologi Malaysia, Skudai 81310, Johor Bahru, JB, Malaysia
[b] Department of Chemical Engineering, COMSATS Institute of Information Technology, Lahore 54000, Punjab, Pakistan
[c] Chemical and Biological Engineering Department, Missouri University of Science & Technology, Rolla, MO 65409, USA
[d] Centre for Process Integration and Intensification – CPI^2, Research Institute of Chemical and Process Engineering – MÜKKI, Faculty of Information Technology, University of Pannonia, Egyetem u. 10, H-8200 Veszprém, Hungary

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ABSTRACT

Growing population and expanding economies are important causes of increasing global energy demand. In wake of the continuous hike in the petroleum prices, depleting world resources and increased constant threat to planet's environment, the need for environment friendly alternative fuels has augmented many times. Methanol has been in the limelight over the past few years. High production cost, catalyst deactivation, economy of scale, huge energy requirements are the leading bottlenecks, which should be resolved to move towards the cleaner production. To address the issues, various reactors and their configurations have been modelled over years and the need to summarise all these efforts seems obligatory. One-dimensional to three-dimensional models for traditional packed bed reactors to processes for direct conversion of natural gas to methanol is available in literature. The presented study is an attempt to compile most of these efforts in order to guide future work in this area for cleaner and healthier environment.

1. Introduction

World economy relies heavily on energy resources and their abundance. The average rate of global energy use, in terms of power equivalent, was about 1 TW in 1990 and doubled by 1955. It increased to 12 TW by 1999 (Reay et al., 2008) and was projected to attain about 18 TW in 2012 (US Energy Information Administration, 2011). In terms of global annual energy use, the equivalent value projected for 2012 would be about 160,000 TWh or 570 × 10^6 TJ. Till 2006, 16% growth in primary energy use was recorded worldwide and still growing from that time. The statistics demonstrate heavy reliance of world economy on energy resources and their still considerable availability. Fossil fuels have remained the basic source of energy for centuries, whose demand has increased noticeably during the past decades. More than 80% of global energy demand is still met by fossil fuels due to their abundance, affordability and availability (Kumar et al., 2011). The world fossil fuel resources are depleting and the cautions issued by environmental protection agencies around the globe have stricken energy-famished nations. The oil crisis of 1970s paved way for alternative energy sources and also stressed on the need of effective utilisation of available resources. Even though crude oil prices touched alarming levels at the start of this century, energy supply has been and in all likelihood will continue to be dominated by fossil fuels (Browne et al., 2012).

The increasing dependency and subsequent demand of petroleum and its by-products revolutionized the world but at the same time, this rapid industrialisation caused many environmental problems (Benhelal et al., 2013). They have been various options how to deal with this problem under investigation (Munir et al., 2012). Energy related CO_2 emissions around the globe have increased by 38.14% from 21.5 × 10^9 t to 29.7 × 10^9 t between 1990 and 2007 (U.S. Energy Information Administration, 2010). The 2012 figure already reached 35.6 × 10^9 t (Sikdar, 2013). The ever-increasing interest risk of climate change is a stiff challenge for global society. According to Kyoto Protocol, the conference of the parties has agreed that by committed period 2008–2012, developed countries shall be legally committed to reduce their collective greenhouse gas (GHG) emissions by at least 5% compared to 1990 levels (Barranon, 2006). The recent Doha United Nations Climate

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[*] Corresponding author. Tel.: +1573 341 4423; fax: +1573 341 4377.
E-mail addresses: zahedig@mst.edu, grzahedi@yahoo.com (G. Zahedi).

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Change Conference (2012) reached an agreement to extend the life of the Kyoto Protocol, which would expire at the end of 2012, until 2020, and to highlight the Durban Platform for Enhanced Action (2011), meaning that a successor to the Protocol is set to be developed by 2015 and implemented by 2020.

Using renewable resources to substitute fossil fuels is one of the technological options to mitigate GHG emissions. With almost 30% (27% in 2007) of the world's total delivered energy being utilised in the transportation sector only – mostly as liquid fuels (U.S. Energy Information Administration, 2010), increasing energy security and CO_2 emissions, both hydrogen and methanol economy may serve as saviours (Olah, 2005). Methanol has edge over hydrogen gas as it is safe liquid. It is easy for storage and distribution; it can be blended with gasoline and can also be used in the direct methanol fuel cells (Masih et al., 2010). There have been some recent developments for sizable proportion of liquid consuming transportation vehicles (cars, trucks, trains, and planes) to use methanol as their energy source (Luyben, 2010).

Methanol can be obtained from multiple sources including biomass and coal but natural gas (NG) is a better choice as a feedstock for methanol. The reason is natural gas is available in high quantities compared to biomass resources and compared to coal; natural gas conversion is environmental friendly process. Production of methanol, dimethyl ether and synthetic fuels from NG has become an important option for exploitation of oil and gas fields, which earlier were not economically viable. This concerns remote gas fields, gas fields without transport infrastructure, and associated gas fields where a total solution for both oil and gas is needed (Kvamsdal et al., 1999). NG, one of the major fossil energy sources has estimated proven gas reserves of 177×10^{12} m^3 of which around 40% are too far from market reach (Velasco et al., 2010). Well-established technologies are available for conversion of NG to synthesis gas (SG) and are widely used in chemical process plants. All over the world, methanol production has risen by 42% from 2001 to 2008 (PCI-Ockerbloom & Co. Inc., 2010). Annual production in 2010 was 45 Mt (Aasberg-Petersen et al., 2011).

The methanol market is in a state of change with some derivatives declining, such as methyl tertiary-butyl ether (MTBE), whilst others are increasing strongly such as biodiesel, gasoline blending, dimethyl ether (DME), Methanol to Olefins and Methanol to Propylene. Demand potential into these new outlets is highly dependent on the cost competitiveness of methanol against traditional alternatives such as liquefied petroleum gas. This in turn is determined by future developments in feedstock prices and the structure of the methanol production base (Chem Systems, 2009/10). Overall world demand for methanol is projected to grow at an average annual rate of 9.8% from 2010 to 2015, with lower growth expected in the industrialised areas of the world where the markets are mature. But none of these facilities suffice to produce and supply the quantities required if SG/methanol were to play an increasing role as a new energy source for road traffic Swain et al. (2011). China has been the largest methanol consuming country, and will increase its share of world consumption from almost 41% in 2010 to about 54% in 2015 (Saade, 2011). With increased demand, it is essential to economise the various available processing technologies. Since the industrial implementation of methanol manufacturing process in 1923, there have been constant efforts to upgrade the technology and to incorporate latest research developments (Lange, 2001).

Methanol is a key chemical intermediate and numerous applications transform it into vital products and commodities that span and drive modern life. Fig. 1 gives an overview of methanol demand by end use. Worldwide, formaldehyde production is the largest consumer of methanol, accounting for almost 32% of world methanol demand in 2011. This is anticipated to fall to 25% by 2016 with Gasoline/Fuel applications becoming the largest demand sector, totalling 31%. The consumption of methanol into direct fuel applications surpassed MTBE as the second largest market for methanol, with almost 11% of global methanol demand; by 2016, it is expected to account for 16%, increasing at an average annual rate of nearly 20%. Acetic acid/anhydride and MTBE each share 10% of methanol market volume (Saade, 2011). Methanol to Olefins (MTO) and methanol to propylene (MTP) demand is anticipated to become a high growth sector, rising from 6% of end use demand in 2011 to 22% by 2016, the vast majority of which is forecast to take place in China (Johnson, 2012). Other uses of methanol include wastewater de-nitrification, hydrogen carrier for fuel cells, transesterification of vegetable oils for biodiesel production and electricity generation (Biedermann et al., 2006). There are thousands more products that also touch our daily lives in which methanol is a key component.

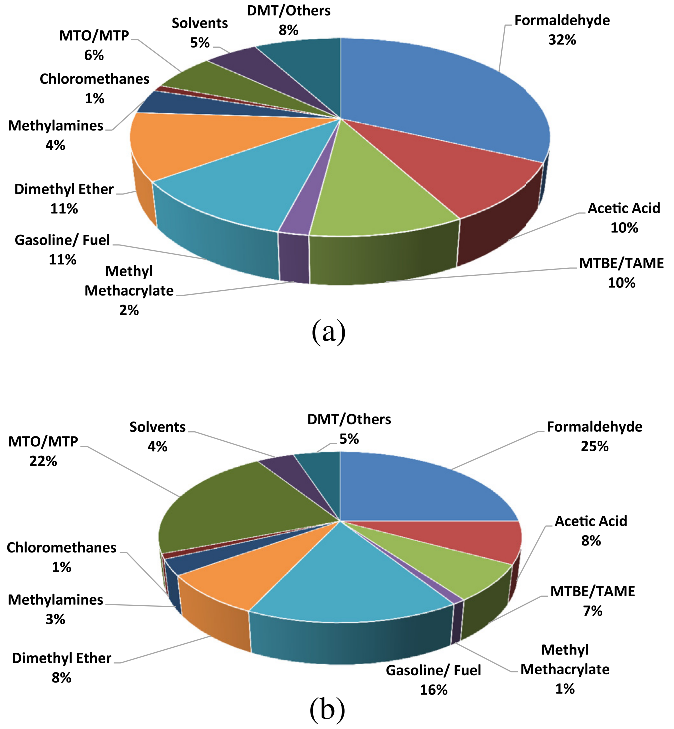

Fig. 1. Current and future methanol demand by end use (a) 2011 demand 55.4×10^6 t (b) 2016 demand forecast 92.3×10^6 t (Johnson, 2012).

Methanol production is today a mature technology and literature covers almost every aspect of its process. High-energy inputs, subsequent installation and maintenance cost render further investment in the field of methanol unless new, improved and efficient processes are not developed. Additionally the process has cleaner production problems associated with deactivation of the catalyst. Existing models only address individual steps or consider localised problems and the need to model the broader canvass is obligatory or imperative.

The main objective of this paper is to highlight the problems associated with mass production of methanol and compile the efforts put in by scientists and researchers to overcome them all in the field of modelling and optimisation. The environmental benefits of utilising methanol for CO_2 reduction shall also be discussed. Hereafter, methanol production process and its challenges are detailed briefly, followed by description of various kinetic, catalyst deactivation and process models. Next is discussion on the application of different reactor types and their models to methanol synthesis for process improvement. This is followed by details of solved optimisation problems and finally the conclusion is presented.

Table 1
Methanol technology suppliers (Cifre and Badr, 2007).

Technology supplier	Temperature (°C)	Pressure (bar)	Notes
ICI (Synetix)	210–290	50–100	Currently licenses four types of reactors: Arc, Tubular Cooled, Isothermal Linde, and Toyo
Lurgi	230–265	50–100	Tubular, isothermal reactor
Mitsubishi	235–270	50–200	Tubular, isothermal reactor
Kellogg			Spherical reactor geometry
Linde AG	240–270	50–150	
Haldor–Topsoe	200–310	40–125	To the date of the cited publication, no commercial plants based on this process.

2. Methanol synthesis technologies

One of the most difficult problems in designing methanol synthesis reactor is removal of reaction heat. Precise temperature control is an additional constraint in the solution of this problem, as excessive temperatures largely affect catalyst life. Tijm et al. (2001) reviewed the development of methanol process and reactor technologies, and broadly classified them into two categories, namely, the gas phase and liquid phase processes. Table 1 shows main technology suppliers and the operating conditions of methanol synthesis.

2.1. Methanol production process

Methanol is typically produced in a three-step process: SG preparation, methanol synthesis and product separation/purification (Fig. 2). SG may be obtained by reforming of NG and liquid hydrocarbons or gasification of coal and biomass. The most widely used route is steam reforming of NG – more than 75% (Cifre and Badr, 2007) commonly referred to as Methane Steam Reforming (MSR).

2.1.1. SG preparation section

SG is a mixture of carbon monoxide (CO), CO_2 and hydrogen (H_2). Its preparation is the most important part in a gas conversion plant both in terms of investment and operating cost. In a typical reformer, NG is reacted with steam over a Ni/Al_2O_3 catalyst to produce SG by the two endothermic steam-reforming reactions of methane. Exothermic water gas shift reaction also takes place in parallel (Ali Alizadeh and Jalali-Farahani, 2007):

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2 ... \Delta H_r = 8.630 \times 10^5 \text{ kJ/kmol} \quad (1)$$

$$CH_4 + 2H_2O \Leftrightarrow CO_2 + 4H_2 ... \Delta H_r = 6.904 \times 10^5 \text{ kJ/kmol} \quad (2)$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2 ... \Delta H_r = -1.7196 \times 10^5 \text{ kJ/kmol} \quad (3)$$

It is obvious that reactions (1) and (2) are highly endothermic and therefore carried out in an NG fired multi-tubular furnace reactor at around 900 °C and pressures of 15–30 bar in gas phase. Schematic of a typical steam reformer is shown in Fig. 3. Natural gas mixed with purge gas is used to fire reformer furnace while excess heat is used to generate steam used in the reforming reactions. The reforming reactions are equilibrium limited and lead to gas expansion (Aasberg-Petersen et al., 2011). Hence, the reactions are favoured at low pressure and high temperature.

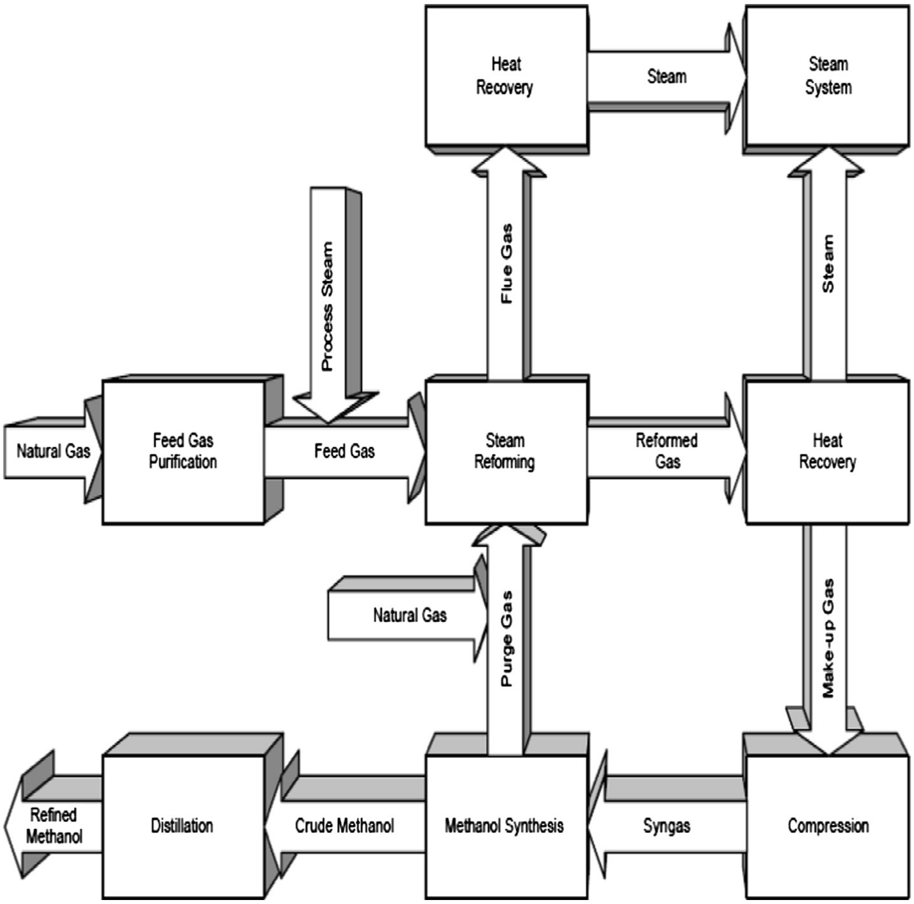

Fig. 2. Processing steps in conventional methanol production process (Fitzpatrick, 2000).

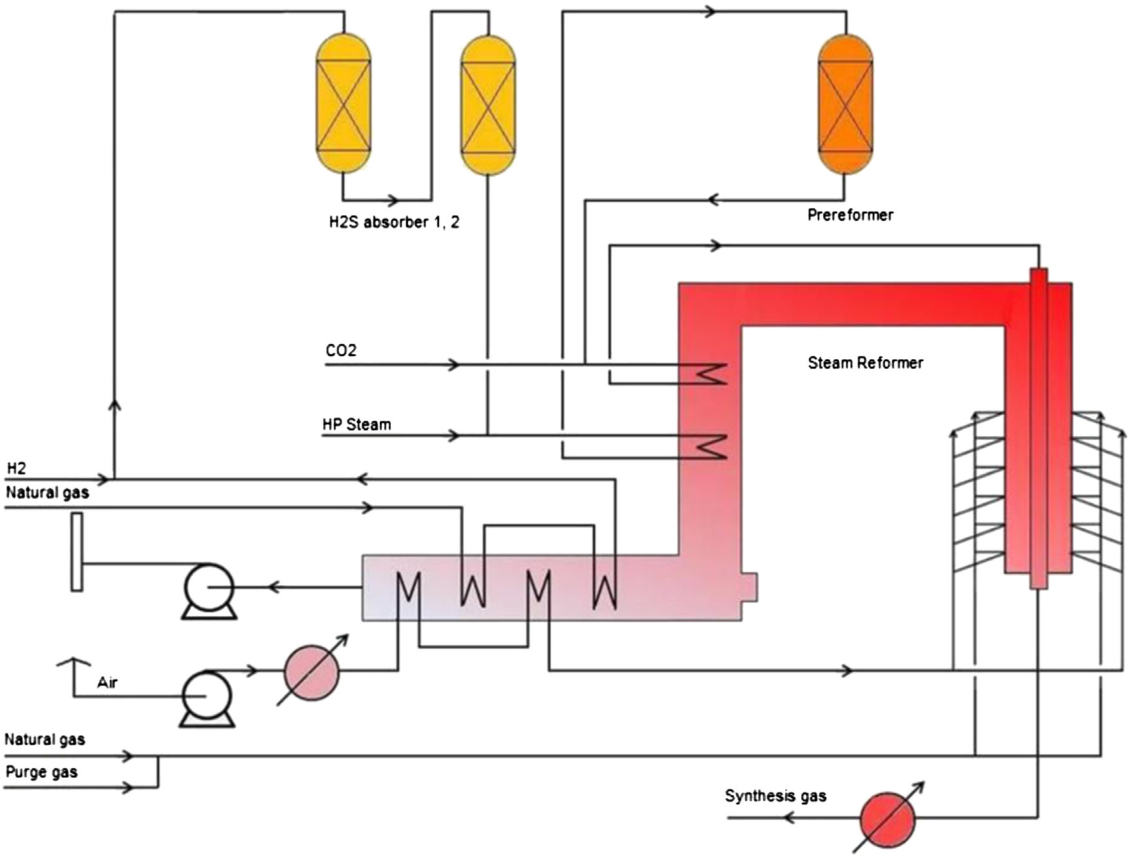

Fig. 3. Process flow diagram of a typical MSR (Tarin, 2009).

The studies on catalysts reveal nickel (Ni) as the best choice owing to stability, cost and fast turnover rates (York et al., 2007). Large catalyst size is preferred due to high flow rate in the usual application (al-Qahtani, 1997). Steam to carbon ratio is kept in excess to the stoichiometric and equilibrium requirement in order to prevent carbon soot formation on the catalyst. About 90–92% (Lange, 2001) of CH_4 is converted to CO_2, CO and H_2. High heat content of SG is used to preheat reformer feed gas and is also utilised to generate high-pressure steam. In this way, overall thermal efficiency of the fired duty approaches 90–97% as only 50% (Wesenberg, 2006) of the fired energy is directly transferred to reactor tubes. The increased demand for large production plants for methanol requires construction of efficient steam reformers with large production capacities (Adris et al., 1991).

2.1.2. *Methanol synthesis section*

The high-pressure process, which was first developed by BASF in 1923 (Tijm et al., 2001), remained the dominant technology for over 45 y. The original high-pressure process was operated at 250–350 bar and 320–450 °C employing a relatively poison (sulphur and chlorine contamination) resistant catalyst, ZnO/Cr_2O_3. The process required momentous investment in the plant design and operating costs for thick walled vessels and considerable compression energy. The ability to produce sulphur free SG and formulation of a new and more active Cu-based catalyst paved way for low-pressure process developed by ICI in 1960s. The process operates at pressures between 50 and 100 bar and temperature range of 200–300 °C (Öztürk and Shah, 1985). The equilibrium limited methanol synthesis reactions are favoured at low temperature but this has adverse effect on catalyst activity. Persistent higher temperatures increase activity of the catalyst at the cost of forming products such as dimethyl ether, higher alcohols, methyl formate and acetone. To ensure catalyst activity and effective use of reaction heat, methanol converters are operated at temperature in the range of 200–300 °C (Malhotra, 2012).

Low-pressure process was the only process employed in the market by 1999. Depending upon the process technology employed, SG may be washed, compressed and heated before entering the methanol synthesis loop. This fresh feed is mixed with recycled unreacted SG and sent to methanol converter where following reactions (Raudaskoski et al., 2009) take place:

$$CO + 2H_2 \leftrightarrow CH_3OH ... \Delta H^\circ = -90.77 \text{ kJ/mol} \quad (4)$$

$$CO_2 + 3H_2 \leftrightarrow CH_3OH + H_2O ... \Delta H^\circ = -49.58 \text{ kJ/mol} \quad (5)$$

$$CO_2 + H_2 \leftrightarrow CO + H_2O ... \Delta H^\circ = +41.19 \text{ kJ/mol} \quad (6)$$

CO reduction is an exothermal process limited by equilibrium and favoured at low temperatures in gas phase. To achieve a reasonable industrial conversion rate, use of specific catalyst and high pressure is mandatory in order to balance out mole decrease during the synthesis (Manenti et al., 2011a). The reaction is carried out on copper oxide, zinc oxide, and alumina ($CuO/ZnO/Al_2O_3$) catalyst. Selectivity of the catalyst towards methanol is quite high, however, for commercial plants; per pass conversion is low necessitating costly recycle. Fig. 4 shows a typical methanol synthesis section.

2.1.3. *Separation and purification section*

The produced methanol contains water, dissolved gases and small amount of H_2. Under normal operating conditions, only small

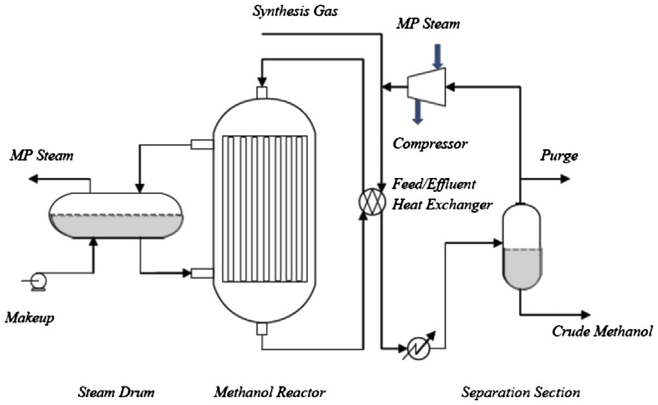

Fig. 4. A typical methanol production unit (Wilhelm et al., 2001).

amount of by-products exist in the outlet stream. These impurities are to be removed in the methanol purification section. This section normally consists of two to three distillation columns. The physically dissolved gases are flashed off in a flash vessel while low boiling impurities are removed in a pre-run column (Zahedi, 2005). The stabilised methanol is distilled in a two-stage system first under pressure and second at atmospheric pressure to obtain a specific product. The higher boiling point components are removed in the two stage distillation columns. Process flow sheet of such a section of methanol plant is shown in Fig. 5.

2.2. Major challenges

The SG routes are highly efficient, but capital intensive because they involve exchange of energy in the reformers and heat recovery units. For methanol synthesis, conversion per pass and yield are important factor eyeing long-term catalyst deactivation; and it should tolerate the normal SG composition, otherwise potential savings are compensated for by increased cost in the SG manufacture (Aasberg-Petersen et al., 2001). Baliban et al. (2013) estimated that in most applications of synthesis gas such as methanol, Fischer–Tropsch synthesis, about 60–70% of the cost of the overall process is associated with SG generation, 20–25% with methanol synthesis step and the rest with final product upgrading and purification.

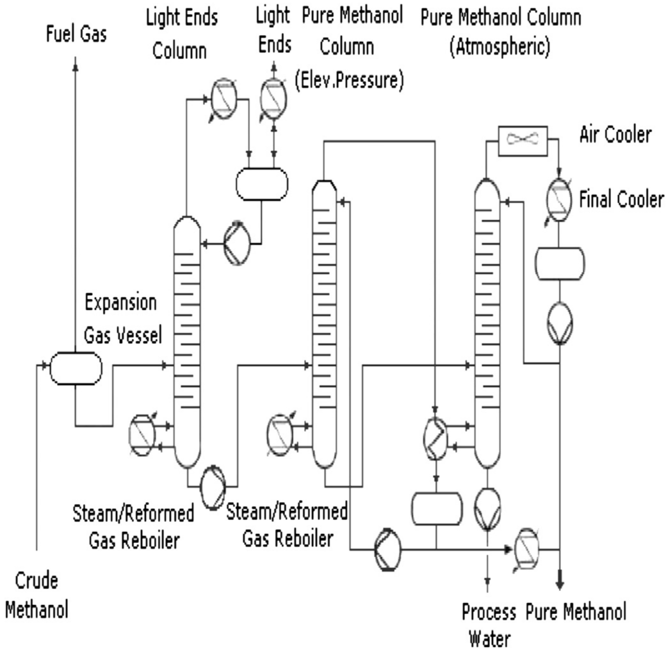

Fig. 5. Process flow diagram of a 2-stage methanol distillation (Higman, 1995).

2.2.1. High-energy demand

CH_4 molecule is very stable, with a C–H bond energy of 439 kJ/mol and it is resistant to many reactants (Navarro et al., 2007). The industrial chemical processes involving methane, e.g. MSR and methane pyrolysis are highly endothermic and consequently consume a large amount of heat. NG combustion is one of the main sources of high thermal energy requirements of the process. High flame temperatures lead to substantial heat loss and thermal nitrogen oxides emissions (Ismagilov et al., 2001). Conventional MSR units with methane as fuel have thermal efficiency of 63–64% (Zeman and Castaldi, 2008).

SG preparation section is the most expensive – 60% of the large-scale plant's total investment (Aasberg-Petersen et al., 2001) of the three methanol production process sections. It is also responsible for the largest part of the energy conversion in the plant (Aasberg-Petersen et al., 2004). Fuel firing, heating, cooling and excess steam contribute to large heat transfer duties and large investments (Lange, 2001) which is the offset to be addressed for future energy economy. Therefore, there is great interest in optimising process schemes as well as in developing new technologies which can decrease capital cost of SG generation (Velasco et al., 2010). Riaz et al. (2011) have investigated the effect of inert gas step addition on energy utilization and conversion of methane. The authors studied the effect of six different inert gases. The results have shown marked decrease in reactor outlet temperature at increased methane conversions.

2.2.2. Catalyst deactivation

A number of factors influence the deactivation of MSR catalyst such as sintering, poisoning and carbon formation. NG usually contains small amounts of sulphur components and a desulphurization unit is installed prior to MSR. Nickel is most susceptible to sulphur poisoning of the group VIII metals. Apart from sulphur, presence of arsenic, lead, phosphorous, silica and alkali metals also considerably reduce catalyst activity (Aasberg-Petersen et al., 2011).

Deactivation of nickel catalysts by carbon formation is a significant problem in methane reforming caused by fouling of the Ni surface, blockage of the pores of the catalytic particle and disintegration of the support material (Pedernera et al., 2007). Carbon formation is avoided through proper design of the catalyst and MSR process (Aasberg-Petersen et al., 2011). The catalyst activity is affected by coking reactions. These occur parallel to reforming reactions and poison the catalyst surface, hence reducing its activity. The coking reactions are the CO reduction (Beggs reaction), methane cracking and Boudourd reaction (Navarro et al., 2007):

$$CO + H_2 \Leftrightarrow C_{(s)} + H_2O \tag{7}$$

$$CH_4 \Leftrightarrow C_{(s)} + 2H_2 \tag{8}$$

$$2CO \Leftrightarrow C_{(s)} + CO_2 \tag{9}$$

The phenomenon is more pronounced in operations involving low steam to carbon ratios or at conditions aiming at low H_2/CO ratios, such as methanol synthesis (Lukyanov et al., 2009).

Among other challenges faced by methanol industry is catalyst deactivation that is mainly due to chemical poisoning and thermal sintering. The impurities like sulphur, chlorine, heavy metals, oil and steam are poisonous to activity and reduce life of methanol reactor catalyst (Moulijn et al., 2001). Negative impacts of poisons are taken care of by introducing gas-cleaning steps prior to steam reforming. The movement of atoms and crystals to form agglomerates is referred to as sintering and it decreases active surface area by increasing crystal size. While sintering of copper occurs slowly at methanol reaction temperature, the catalyst has a lifetime of several years.

In order to keep up with the production rate and initial fast deactivation, working temperature is usually increased. This accelerates catalyst deactivation rate and disturbs the thermal equilibrium of the system. The thermodynamics of the system suggest that the reactions should be carried out at low temperatures and excessive heat be removed effectively and efficiently. Low conversion per pass, higher recycling cost, insufficient selectivity of catalyst, and scale-up issues are only some of the difficulties of this process (Løvik, 2001).

2.2.3. Stoichiometric number

Since SG is a raw material for a number of petrochemicals, its composition at the exit of the reformer varies accordingly. It is often characterized by H_2/N_2 ratio (ammonia synthesis), H_2/CO ratio or stoichiometric number (SN) or module (Aasberg-Petersen et al., 2011). In the synthesis of methanol, both CO and CO_2 are linked by shift reaction, so SG has the same stoichiometry as methanol. Hence, SG composition is characterised by SN:

$$SN = \frac{H_2 - CO_2}{CO + CO_2} \tag{10}$$

Here, H_2, CO and CO_2 refer to their respective concentrations in SG. Makeup gas with SN <2 means excess carbon oxides relative to H_2, which leads to increased formation of by-products or need of removal of certain fractions of CO_2 via shift step. The gas with SN >2 would mean a surplus of hydrogen and carbon deficiency that is typical of steam reforming. This implies an increased recycle rate resulting in less efficient and more expensive plant (Tjatjopoulos and Vasalos, 1998). Løvik et al. (1998) have mentioned an optimal value of SN $= 2.05$ meaning a slight excess of hydrogen. Ribeiro et al. (2012) proposed three different pressure swing adsorption cycles to be integrated in the methanol plant. SG from reformer if passed through any of these cycles brings the SN to ideal methanol feed requirement, i.e., 2.1.

3. Modelling as solution

Environmentally benign technical solutions, sustainability, efficient plant design, optimisation of process schemes and development of new technologies are only few of the methods that may be adopted to hold decrease in the capital cost of any process (Velasco et al., 2010). The application of modelling and simulation to chemical reactors is handy for design, development, operation and improvement of chemical reactors in their online performance. Theoretical and experimental studies for packed bed reactors are in practice for decades. Heat and mass transfer mechanisms, their empirical correlations, catalyst activities, etc. have been the focal point and the results show a scattered behaviour; probably because of variations in experimental methods and techniques to follow different set of assumptions. In the following sections, some of the significant process models for methanol preparation shall be discussed with special emphasis on kinetic and catalyst deactivation models.

3.1. Kinetic models

Various kinetic models are available in the literature owing to trials of different catalyst and reactor configurations. The types of reaction kinetics include: power law kinetics, elementary kinetics, Langmuir–Hinshelwood kinetics and polymerization kinetics (Salmi et al., 1992).

Skrzypek et al. (1995) reviewed some of the earlier kinetic models including their own efforts for determining the reaction mechanism. Leonov et al. (1973) were the first one to develop kinetic model of $Cu/ZnO/Al_2O_3$ catalyst for methanol synthesis. The model considered CO as the only reactant and did not account for CO_2 present in the feed. Prior to 1982, most of the kinetic expressions only accounted for concentration or partial pressure of CO and H_2 (Chinchen et al., 1988). The reaction equations (4)–(6) depict that first equation can be obtained by algebraic solution of the other two equations, making CO as the only contributor of carbon in methanol. This forms the basis of a long debate regarding the major reactant. The scientists have contrasting opinions concerning the major component responsible for the conversion of SG to methanol. CO_2 consumes some of H_2 as water, which accelerates deactivation of the catalyst but it is also established that small amount of CO_2 in the feed help promote CO conversion to methanol (Biedermann et al., 2006). Earlier kinetic studies considered CO as the only reactant and later CO_2 alone was considered as the main and only reactant (Nerlov et al., 2000; Raudaskoski et al., 2009). It is only until recent isotopic studies reveal that both CO and CO_2 are responsible for the reaction (van Lier et al., 2008). The mechanistic studies (Fujita et al., 1995) believe that the reaction rates may be different and may be that can be a reason for this conflict. Wang et al. (2010) have shown both CO and CO_2 as primary source of carbon in methanol by in situ FT-IR studies for methanol synthesis using $Cu-ZnO-Al_2O_3$ catalyst. Table 2 summarises few of those models which considered both CO and CO_2.

It may also be seen that in most of the earlier studies either reverse water gas shift reaction or CO hydrogenation reaction was not considered. Villa et al. (1985) employed a mixture of CO and CO_2 with the basic assumption of CO as the main source of methanol. The rate expressions developed include an inhibition term associated with CO_2 adsorption. Bos et al. (1989) reported kinetic study based on CO and H_2 using commercial BASF catalyst. However, no single rate expression was deduced. Graaf et al. (1988a) considered all the three reactions with a dual site adsorption mechanism. It was assumed that both CO and CO_2 adsorb on same sites competitively. Rahimpour et al. (1998) developed a kinetic model for deactivated Cu/ZnO catalyst considering CO and CO_2 hydrogenation reactions. Computer simulation results highlight the role of CO_2 concentration in the feed and of water in deactivation of the catalyst. Pisarenko and Pisarenko (2007) in their study of kinetics of methanol synthesis discarded the published kinetic models on grounds of accuracy of constant estimation. Numerical values of kinetic constants were determined experimentally and used in the designing of methanol synthesis reactor. The unit consists of three single pass shell and tube reactors without feed recirculation. The proposed unit reduces the product cost by 15–20% and considers elimination of one distillation column with higher quality level of methanol. Lim et al. (2009) have considered four reactions, additional being DME formation reaction using different catalyst ($Cu/ZnO/Al_2O_3/ZrO_2$). However, the final expressions do not include any term related to this reaction. The model has not yet been tested for any study.

Commercial catalyst works well within a narrow range of CO_2/CO ratio. Numerous catalysts, e.g., fibrous Cu/Zn/Al/Zr (An et al., 2009), $CuO/ZnO/Al_2O_3$ (Baltes et al., 2008), Ga_2O_3-Pd/silica (Chiavassa et al., 2009), $Cu/ZnO/Al_2O_3/ZrO_2$ (Lim et al., 2009), Cu(1 0 0) and Cu(1 0 0) modified by Ni and Co (Nerlov et al., 2000), have been tried and tested in order to curb and minimise deactivation rate and to enhance selectivity and yield of methanol. The methanol synthesis at low temperature, a new process, from $CO/CO_2/H_2$ on Cu/ZnO using catalytically active alcohol promoter is supposed to follow alkyl formate

Table 2
Summary of primary kinetic models for methanol synthesis.

Authors	Catalyst	Temp. (K)	Press. (bar)	Reaction(s)	Kinetic rate equations
Klier et al. (1982)	CuO–ZnO	498–523	75	$CO + 2H_2 \leftrightarrows CH_3OH$ $CO_2 + 3H_2 \leftrightarrows CH_3OH + H_2O$ $A_{red} + CO_2 \leftrightarrows A_{ox} + CO$ redox reaction (3) is at equilibrium	$r_1 = k_1\left[1 + \frac{1}{K^{eq}_{redox}} \frac{P_{CO}}{P_{CO_2}}\right]^{-3} \frac{K_{CO} K^2_{H_2} (P_{CO}P^2_{H_2} - P_{CH_3OH}/K^{eq}_1)}{1+ K_{CO} P_{CO}+ K_{CO_2} P_{CO_2} + K_{H_2} P_{H_2}}$ $r_2 = k_2 \left(P_{CO_2} - \frac{1}{K^{eq}_2} \frac{P_{CH_3OH}P_{H_2O}}{P^3_{H_2}}\right)$
Graaf et al. (1988a)	$CuO/ZnO/Al_2O_3$ Haldor Topsoe Mk 101	483–518	15–50	$CO + 2H_2 \leftrightarrows CH_3OH$ $CO_2 + 3H_2 \leftrightarrows CH_3OH + H_2O$ $CO_2 + H_2 \leftrightarrows CO + H_2O$	$r_1 = \frac{k_1 K_{CO}(a_{CO}a^{3/2}_{H_2} - a_{CH_3OH}/a^{1/2}_{H_2}K^{eq}_1)}{(1+ K_{CO}\ a_{CO}+ K_{CO_2}\ a_{CO_2})[a^{1/2}_{H_2} + (K_{H_2O}/k^{1/2}_{H_2})\ a_{H_2O}]}$ $r_2 = \frac{k_2 K_{CO_2}(a_{CO_2}a_{H_2} - a_{H_2O}a_{CO}/K^{eq}_2)}{(1+ K_{CO}\ a_{CO}+ K_{CO_2}\ a_{CO_2})[a^{1/2}_{H_2} + (K_{H_2O}/k^{1/2}_{H_2})\ a_{H_2O}]}$ $r_3 = \frac{k_3 K_{CO_2}(a_{CO_2}a^{3/2}_{H_2} - a_{CH_3OH}a_{H_2O}/a^{3/2}_{H_2}K^{eq}_3)}{(1+ K_{CO}\ a_{CO}+ K_{CO_2}\ a_{CO_2})[a^{1/2}_{H_2} + (K_{H_2O}/K^{1/2}_{H_2})\ a_{H_2O}]}$
McNeil et al. (1989)	BASF S3-85	483–518	28.9–43.8	$CO + 2H_2 \leftrightarrows CH_3OH$ $CO_2 + 3H_2 \leftrightarrows CH_3OH + H_2O$	$r_1 = \frac{k'_1 K_{CH}K^2_{H_2}K^2_H K_{CO}\ (P_{CO}P^2_{H_2} - P_{CH_3OH}/K^{eq}_1)}{1+K_{CH}\ K^{3/2}_{H_2}K^{3/2}_H K_{CO}P_{CO}P^{3/2}_{H_2} + K_{CO_2}\ P_{CO_2} + K'_{H_2} P_{H_2}}$ $r_2 = \frac{k''_1 K_{CHO_2}K_{H_2}K_H K_{CO_2}\ (P_{CO_2}P_{H_2} - P_{CH_3OH}P_{H_2O}/(P^2_{H_2}K^{eq}_2))}{1+K_{CHO_2}\ K^{1/2}_{H_2}K^{1/2}_H K_{CO_2}P^{1/2}_{H_2} + K''_{CO_2}\ P^2_{CO_2} + K_{H_2O}P^3_{H_2O}}$
Skrzypek et al. (1991)	$CuO–ZnO–Al_2O_3$ Commercial Blasiak's catalyst	460–500	30–90	$CO_2 + 3H_2 \leftrightarrows CH_3OH + H_2O$ $CO_2 + 2H_2 \leftrightarrows CO + H_2O$	$r_1 = k_1\ K^2_{H_2}K_{CO_2}\left[\frac{P^2_{H_2}P_{CO_2} - \frac{P_{CH_3OH}P_{H_2O}}{K^{eq}_1 P_{H_2}}}{(1+ K_{H_2}P_{H_2} + K_{CO_2}P_{CO_2} + K_{CH_3OH}P_{CH_3OH} + K_{H_2O}P_{H_2O} + K_{CO}P_{CO})^3}\right]$ $r_2 = k_2\ K_{H_2}K_{CO_2}\left[\frac{P_{H_2}P_{CO_2} - \frac{P_{CO}P_{H_2O}}{K^{eq}_2}}{(1+ K_{H_2}P_{H_2} + K_{CO_2}P_{CO_2} + K_{CH_3OH}P_{CH_3OH} + K_{H_2O}P_{H_2O} + K_{CO}P_{CO})^2}\right]$
Coteron and Hayhurst (1994)	$Cu_{70}Zn_{30}$ and $Cu_{70}Zr_{30}$	473–523	10	$CO + 2H_2 \leftrightarrows CH_3OH$ $H_2 + CO + CO_2 \leftrightarrows CH_3OH + H_2O$	$r_1 = \frac{k_{11}K_{CO}K^2_H K_{CH}P_{CO}P^2_{H_2}}{1+ K_{CO}P_{CO} + K_{CO}K^{3/2}_H K_{CH}P_{CO}P^{3/2}_{H_2}}$ $r_2 = \frac{k_{12}K_{CO_2}K_H K_{HCO_2}P_{CO_2}P_{H_2}}{1+ K_{CO_2}P_{CO_2} + K_{CO_2}K^{1/2}_H K_{HCO_2}P_{CO_2}P^{1/2}_{H_2} + \frac{K_{CO_2}P_{CO_2}}{K_{CO}P_{CO}}}$
Bussche and Froment (1996a)	$Cu/ZnO/Al_2O_3$ catalyst	180–280 °C	15–51	$CO_2 + 3H_2 \leftrightarrows CH_3OH + H_2O$ $CO_2 + H_2 \leftrightarrows CO + H_2O$	$r_{MeOH} = k'_{5a}K'_2K_3K_4K_{H_2}P_{CO_2}P_{H_2}\left(1 - \frac{1}{K^*_1}\frac{P_{H_2O}P_{MeOH}}{P^3_{H_2}P_{CO_2}}\right)\beta^3$ $r_{RWGS} = k'_1 P_{CO_2}\left(1 - \frac{1}{K^*_3}\frac{P_{H_2O}P_{MeOH}}{P^3_{H_2}P_{CO_2}}\right)\beta$ Where, $\beta = \frac{1}{1+\left[\frac{K_{H_2O}}{K_8K_9K_{H_2}}\frac{P_{H_2O}}{P_{H_2}} + \sqrt{K_{H_2}\ P_{H_2}} + K_{H_2O}\ P_{H_2O}\right]}$
Chiavassa et al. (2009)	Ga_2O_3–Pd/Silica	508–538	10–40	$CO_2 + 3H_2 \leftrightarrows CH_3OH + H_2O$ $CO_2 + H_2 \leftrightarrows CO + H_2O$	$r_{MeOH} = \frac{k''_3\ P_{CO_2}\ \alpha^2}{D^2}[1 - (P_{MeOH}\ P_{H_2O}/P^3_{H_2O}\ P_{CO_2}\ K_{R_1}\ (\alpha/\alpha_{eq})^6\ )]$ $r_{RWGS} = \frac{k''_{12}\ P_{CO_2}\ \alpha}{D}[1 - (P_{MeOH}\ P_{H_2O}/P_{H_2}\ P_{CO_2}\ K_{R_2}\ (\alpha/\alpha_{eq})^2\ )]$ Where, $D = 1 + \sum^8_{i=1} g_i(\alpha)$; and, $\alpha = [H^*_-]/[*]$
Lim et al. (2009)	$Cu/ZnO/Al_2O_3/ZrO_2$	503–553	50	$CO + 2H_2 \leftrightarrows CH_3OH$ $CO_2 + 3H_2 \leftrightarrows CH_3OH + H_2O$ $CO_2 + H_2 \leftrightarrows CO + H_2O$ $2CH_3OH \leftrightarrows CH_3OCH_3 + H_2O$	$r_A = \frac{k_A\ K_{CO}K^{0.5}_{H_2}\ K_{CH,CO}\ (P_{CO}\ P^2_{H_2} - P_{MeOH}/K_{p_A})/P^{1.5}_{H_2}}{(1+ K_{CO}\ P_{CO})(1+ K^{0.5}_{H_2}\ P^{0.5}_{H_2} + K_{H_2O}\ P_{H_2O})}$ $r_B = \frac{k_B\ K_{CO_2}K^{0.5}_{H_2}\ (P_{CO_2}\ P_{H_2} - P_{CO}\ P_{H_2O}/K_{p_B})/P^{0.5}_{H_2}}{(1+ K_{CO}\ P_{CO})(1+ K^{0.5}_{H_2}\ P^{0.5}_{H_2} + K_{H_2O}\ P_{H_2O})\ (1+ K_{CO_2}\ P_{CO_2})}$ $r_C = \frac{k_C\ K_{CO_2}K_{H_2}\ K_{CH,CO_2}\ (P_{CO}\ P^3_{H_2} - P_{MeOH}\ P_{H_2O}/K_{p_C})/P^2_{H_2}}{(1+ K^{0.5}_{H_2}\ P^{0.5}_{H_2} + K_{H_2O}\ P_{H_2O})\ (1+ K_{CO_2}\ P_{CO_2})}$

′, ″, * represent parametric values for intermediates catalyst sites.

formation mechanism. The experimentation reveals effect of alcohol structure on reaction activity. The yield and total carbon conversion for 2-propanol (Zhang et al., 2008), 2-butanol (Reubroycharoen et al., 2004), *n*-butanol, ethanol and methanol (Tsubaki et al., 2001) has been studied. It was found that 2-butanol was the most effective alcoholic solvent for this low-temperature process.

Dong et al. (2003) found that copper exposed area can be increased, generating more active copper sites at the surface of the catalyst, by using carbon nanotubes as promoter to Cu–Zn–Al_2O_3 catalyst. The tubes play the role of dispersant for catalyst components, adsorbent, activator and hydrogen reservoir whereby CO/CO_2 hydrogenation reaction rates are enhanced. Peter et al. (2012) reviewed the three basic types of models extensively used in modelling methanol synthesis reactions, namely Power law, Langmuir–Hinshelwood–Hougen–Watson approach and the microkinetic models. All models were found to be valid while Langmuir–Hinshelwood–Hougen–Watson model yields a good fit to experimental data.

3.2. Catalyst deactivation models

The decrease in the activity and/or selectivity of a particular catalyst with time is a continued problem of industrial catalytic processes. It was considered as an inevitable process but it can be slowed or prevented and some of its consequences can be avoided. Prevention of catalyst degradation poses substantial challenges in the design and operation of a large-scale unit. All catalysts deactivate and become less effective with time however, time duration may range from a few seconds to many years. Interestingly a short life does not necessarily mean that the catalyst will not be used. The catalyst volume caters for slow deactivation (see Fig. 6) and as compensatory measure, temperature may be increased which may affect catalyst. Economics of the plant have the last say in decision regarding catalyst activity, selectivity and lifetime.

Moulijn et al. (2001) have reviewed some typical industrial cases of catalyst deactivation highlighting the consequences faced by the catalyst and the process. Table 3 details processes relevant to scope of present study. Sintering, coke formation and poisoning due to presence of certain chemicals/metals reduce catalyst life to some days, as is the case with hydrotreating. Certain modifications in preparation of catalyst and/or process operations help countering deactivation. Feed purification and optimising reaction conditions are some of the good engineering practices. In case of methanol, in order to combat sintering, stabilizers like ZnO are introduced in catalyst while extra care is taken during feed purification.

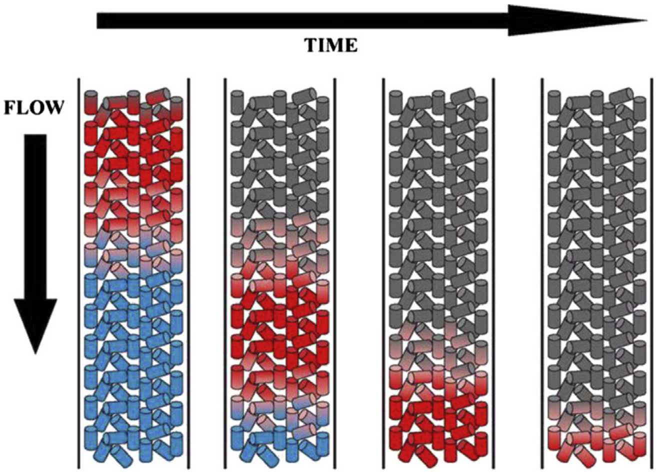

Fig. 6. A schematic representation of a catalyst deactivation front (Jackson, 2006).

Sulphur, chlorine compounds, metal carbonyls, etc., excess CO_2 and water have been reported as potential reasons for catalyst poisoning. Copper is partially oxidized due to adsorbed oxygen and increases the deposition rate of CO_2. Partial oxidation of active copper metal site depends upon CO_2/CO ratio. It has been observed that CO_2 rich feed gas leads to higher deactivation rate, but independent studies have shown that presence of water produced because of water gas shift reaction is the cause of sintering (Keskitalo et al., 2007). However, the major cause of catalyst deactivation, reported extensively in literature, is thermal sintering, because of poor heat transfer mechanisms in the reactor. The thermal misbalance causes clustering of copper sites and reduced effective area (Tijm et al., 2001).

Deactivation is usually modelled using Simple Power Law Expression (SPLE) (Bartholomew, 2001):

$$-\frac{d\left(D/D_0\right)}{dt} = k_s\left(\frac{D}{D_0}\right)^n \tag{11}$$

where, k_s = sintering rate constant, D_0 = initial dispersion, n = sintering order, vary from 3 to 15.

The sintering rate constant depends upon the temperature and varies according to Arrhenius equation as

$$k_s = k_s \exp\left(\frac{E_{act}}{RT}\right) \tag{12}$$

It is clear that the value of k_s may vary with sintering time and hence with dispersion. It is therefore not possible to quantitatively measure kinetic parameters from this rate expression because they are functions of time and Eq. (12) seems inadequate to cope with the intricacies of sintering kinetics. Fuentes and Gamas (1991) have presented a slightly different expression, known as generalized power law expression, to help understand sintering in a better way.

$$-\frac{d\left(D/D_0\right)}{dt} = k_s\left(\frac{D}{D_0} - \frac{D_{eq}}{D_0}\right)^m \tag{13}$$

The term D_{eq}/D_0 has been added to account for asymptotic approach observed in the typical dispersion–time curves. Various parameters in Eq. (13) are functions of time; and it is possible to quantify various effecting parameters (Forzatti and Lietti, 1999). Sintering order, m, is found to be either 1 or 2. Bartholomew (2001) has applied this model for steam-reforming (Ni/Al_2O_3) catalyst and showed promising results compared to some of the other commercial catalysts.

Number of researchers validated these relations using different catalysts, operating conditions and reactors. Roberts et al. (1993) used $Cu/ZnO/Al_2O_3$ in a gas sparged slurry reactor operating at 250 °C and 53 bar. They found that deactivation rate for methanol synthesis is first order. Sahibzada et al. (1997) and Sun et al. (1999) employed an internal recycle gas phase flow reactor with Pd-promoted $Cu/ZnO/Al_2O_3$ operating at a temperature of 250 °C and 50 bar pressure. During the initial period of 10 h, deactivation of the order of $n \approx 10$ is fitted as:

$$-\frac{dS}{dt} = kS^n \tag{14}$$

where, S is active metal surface area.

Løvik (2001) has reviewed more than seven deactivation models, two of which are listed above and developed a model of his own by adjusting the model of Skrzypek et al. (1984). The latter have used fixed bed gas phase reactor. The final form of the model equation is

$$\frac{da}{dt} = -K_d \exp\left(\frac{-E_d}{R_g}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right) a^5 \tag{15}$$

The values of K_d and E_d have been reported as 4.39×10^{-5} h^{-1} and 9.1×10^4 J/mol.

Hanken (1995) developed model similar to Eq. (15) and has been employed by many researchers. Parvasi et al. (2008) analysed a typical methanol reactor loop with all basic conventional equipment. The analysis was based on an in-depth dynamic model for effective prediction of process variables and their behavioural patterns. The kinetic model of Graaf et al. (1988a) and deactivation model of Hanken (1995), which best fits (Askari et al., 2008) the industrial operating conditions, were adopted. Diffusional effects were considered and hence a couple of equations added in the reactor model equations in the form of effectiveness factor

Table 3
Typical cases of catalyst deactivation and measures taken to counteract it (Moulijn et al., 2001).

Process	Catalyst	Main deactivation mechanism	Time scale of deactivation	Consequences for catalyst	Consequences for process
Catalytic reforming	$Pt/\gamma\text{-}Al_2O_3$	Coke	Months	Alloying	Fixed bed, swing operation, moving bed
Hydrotreating	$Co/Mo/S/Al_2O_3$	Coke	Months	Once through catalyst	Fixed bed, slurry, moving bed
		Metal sulphides	days	Adapted porosity	
Methanol	$Cu/ZnO/Al_2O_3$	Sintering (Cl)	years	Stabilization	Feed purification
Water–gas shift	$Cu/ZnO/Al_2O_3$	Poisoning (S, Cl)	years	Stabilizers (ZnO)	Feed purification
Steam reforming	Ni/Al_2O_3	Coke, whiskers		K, Mg gasification catalysts	Excess steam
Dry reforming	Ni	Coke		S-doping	Excess steam

evaluation using dusty gas model. The models were validated against process plant data spanning a time period of 760 d. Parvasi et al. (2008) observed deviation in CO_2 concentration upon validation against process plant data for their study on the dynamics of methanol synthesis reactions. The effect of CO/CO_2 ratio on catalyst reformulated the original deactivation model as:

$$\frac{da}{dt} = -\left(\frac{CO}{CO_2}\right)^m K_d \exp\left[\frac{-E_d}{R}\left(\frac{1}{T} - \frac{1}{T_R}\right)\right] a^5 \tag{16}$$

where, m is reaction rate parameter.

3.3. Process models

Packed bed reactors are modelled as pseudo-homogeneous or heterogeneous in one- or two-dimensions. In case of pseudo-homogeneous models, the gas phase and the solid (catalyst particles) phase are considered as a single entity with averaged properties for both phases. The reaction rates are calculated from bulk concentrations and temperatures and scaled with effectiveness factors to compensate for the concentration differences between the gas and interior of solid particles. In a heterogeneous model, both phases are present and account for heat and mass transport both between the particles and gas and within the particles. In reactors, heterogeneous models are advantageous to give details of pellet internal concentrations and temperatures, essential for evaluating effectiveness factors and catalyst deactivation (Wesenberg, 2006).

Methanol synthesis, ammonia synthesis, fluid catalytic cracking are typical examples of the role chemical engineering science and field of catalysis have played in creation and development of process industry. Introducing new and innovative ideas is a challenge in process industry. At the beginning, plants were larger because of the economy of scale, but then they became more integrated to achieve a better energy economy (Nielsen, 1995). Even so, growing worldwide competition necessitates major changes in conventional plant design procedures. Table 4 gives an overview of some of the recent simulation studies on methanol briefly mentioning about the sub-models and the techniques used for solution of problems.

Methanol may be produced in a number of reactor types and each one of those has particular limitations. Aasberg-Petersen et al. (2011) have recently proposed a few combinations of steam reforming, auto-thermal reforming and methanol reactor. The new advanced design Lurgi's Mega Methanol project (Lurgi Gmbh, 2010) also permits capacities as high as 2.3 Mt/y. In the following lines, various modelling studies carried out on aforementioned different reactors shall be briefly discussed.

3.3.1. Fixed bed reactors

Conversion of SG to methanol in fixed bed reactors is limited by the reaction equilibrium and high-temperature sensitivity of the catalyst (Rostrup-Nielsen, 2002). Temperature moderation is achieved by recycling large amounts of hydrogen-rich gas, utilizing the heat capacity of H_2 gas and the higher gas velocities to enhance the heat transfer. Theoretical and experimental studies for packed bed reactors are in practice for decades.

Elnashaie and Abdel-Hakim (1988) stressed on the importance of diffusional limitations and its impact on optimisation of fixed bed reactors. The usual practice is to neglect this important limitation. These limitations directly influence actual rate of reaction, consequently conversion, temperature and rate of deactivation along the length of the reactor. Graaf et al. (1990) modelled low-pressure methanol synthesis using commercial Cu–Zn–Al catalyst and showed that commercial size of the catalyst particles exhibit intra-particle diffusion limitations while Lommerts et al. (2000) emphasized that Thiele modulus concept with pseudo-first-order kinetics is capable to predict intra-particle diffusion.

Løvik et al. (1999) developed a dynamic model for methanol synthesis amid catalyst deactivation. In order to address the issue of catalyst deactivation a pseudo steady state two-dimensional heterogeneous reactor model was developed neglecting viscous flow in catalyst pellets and assuming pellets as isothermal. The model is based on the kinetic model of Bussche and Froment (1996a), and the deactivation model of Skrzypek et al. (1991). According to author, the major cause of sintering in this process is temperature and proposed a couple of changes in the synthesis loop.

Rezaie et al. (2005) developed and compared the performance of homogeneous and heterogeneous models eyeing long-term catalyst deactivation. The homogeneous model neglects the gradient between the solid and fluid-phase and the rates expressed in terms of the fluid-phase concentration and temperature. The heterogeneous model on the other hand accounts for both phases and the rates are expressed in terms of the solid-phase temperature and concentration profiles. The reaction rate expressions and deactivation model were adopted from Graaf et al. (1988a) and also from the later work presented by Hanken (1995). Steady state simulation results showed very close behaviour of gas and solid phases. Using methanol production rate as an index, both models show almost similar results under transient conditions. High inlet gas velocity has been quoted as the major reason for gas and solid to behave in a similar manner. At lower gas velocity, the behaviour of both models is appreciably different.

Lengthy, time consuming and costly experiments may be avoided by the use of computer simulation for evolving better understanding of complex methanol synthesis process. The scarcity of catalyst deactivation data is an important factor in the development of an accurate and effective model. For estimation of catalyst performance data, Zahedi et al. (2005a) employed artificial neural network approach. The effect of operating conditions and change in feed compositions on the deactivation rate of catalyst has been predicted in a Hoffmann type differential reactor. The predicted results have been found in close conformity with available short-term data and thus form the basis for future modelling and estimation practices. Noteworthy is the effect of CO_2 concentration in the feed on methanol production rate and catalyst deactivation rate. For feeds with higher CO_2 concentration the deactivation rate increases, while at the same time the concentration of water also increases. This result is in line with our earlier knowledge of CO_2 as a possible cause of deactivation in methanol synthesis. In another effort (Zahedi et al., 2005b) a hybrid artificial neural network model was developed. The model combines both mechanistic model (first principle model) and neural network models. Hybrid model was found smarter than the others in terms of accuracy and robustness. Simulation of existing industrial reactor showed promising results.

Rahimpour (2008) stepped ahead and instead of using conventional single reactor modelled two stage methanol reactors. Feed SG gets heated by removing reaction heat from second reactor and then fed into the main first reactor. The main first reactor is water cooled and operated at relatively higher temperatures (270 °C). The optimised temperature profile showed less catalyst deactivation and increased methanol yield (Askari et al., 2008). Rahimpour and Lotfinejad (2008a) compared the performance of conventional methanol reactor with two-stage auto-thermal reactor in wake of catalyst deactivation. The cooling feed gas in the second reactor has been tested in co-current and counter-current flow arrangement using one-dimensional heterogeneous model (Rahimpour and Lotfinejad, 2008b). In the co-current configuration, the reactor operates at low temperature increasing the catalyst activity and lifetime but at the same time the production rate is compromised. Kordabadi and Jahanmiri (2005) also discussed the

Table 4
Summary of a few modelling efforts on methanol synthesis.

Authors	Objective	Model(s)	Reactor type	Kinetic model used	Catalyst deactivation model used	Methods/Tools used
Løvik (2001)	To study catalyst deactivation using dynamic model	Pseudo-homogeneous & 2-D heterogeneous	Lurgi type fixed bed reactor	Bussche and Froment (1996a)	Modified the Skrzypek model	Used finite difference method and gPROMS (2012)
Šetinc and Levec (2001)	To develop dynamic model for liquid phase methanol synthesis		Slurry reactor	Experimental	Experimental	The model was solved by Berkeley Madonna™ (2012) code, similar to 4th order Runge–Kutta method
Shahrokhi and Baghmisheh (2005)	To design a PID controller based on modelling and simulation results	1-D heterogeneous	Lurgi type fixed bed reactor	Bussche and Froment (1996a)		Partial differential equations were solved using orthogonal collocation using finite difference and nonlinear equations by Guass-Newton & trust region method. Artificial feed forward neural network and adaptive linear kinetic rate Thiele modulus method, employed for faster calculation times.
Rezaie et al. (2005)	To do a comparative study of models for future applications	1-D homogeneous & 1-D heterogeneous	Lurgi type fixed bed reactor	Graaf et al. (1988a)	Hanken (1995)	Gauss-Newton method for steady state and 2nd order modified Rosenbrock (1960) formula for solving set of dynamic equations.
Pisarenko and Pisarenko (2007)	To develop a new process technology	Quasi-homogeneous model	Carberry type flow circulation reactor	Developed their own model with KS-1 type catalyst, operating within the ranges of 1–60 bar and 373–653 K		Cauchy-normal-first-order differential equations are solved using Runge–Kutta method.
Rahimpour and Lotfinejad (2008c)	To make a comparison between conventional and auto-thermal reactor	1-D heterogeneous	Fixed bed reactor in a shell and tube arrangement	Graaf et al. (1988a)	Hanken (1995)	Steady state solution by Gauss–Newton method is followed by Dynamic model, solution to which is sought by Newton's method in Fortran Power station 4.0 numerical.

Table 4 (*continued*)

Authors	Objective	Model(s)	Reactor type	Kinetic model used	Catalyst deactivation model used	Methods/Tools used
Rahimpour and Lotfinejad (2008a)	To study the effect of co- & counter-current modes for auto-thermal rector	1-D heterogeneous	Fixed bed reactor in a shell and tube arrangement	Graaf et al. (1988a)	Hanken (1995)	Steady state simulation using Gauss-Newton method and Dynamic simulation by 2nd order modified Rosenbrock (1960) formula
Parvasi et al. (2008)	Analysis of methanol loop reactor	1-D homogeneous	Lurgi type industrial reactor	Graaf et al. (1988a)	Hanken (1995)	Finite difference approximation, steady state simulation using Gauss–Newton method and dynamic simulation by 2nd order modified Rosenbrock (1960) formula
Elkamel et al. (2009)	To optimize the methanol synthesis process using superstructure modelling	Heterogeneous	Lurgi type fixed bed reactor	Graaf et al. (1988a)		Algebraic equations by Gauss-Newton method and ordinary differential equations (ODEs) by MATLab ODE15s solver (Shampine and Reichelt, 1997).
Rahimpour et al. (2009)	To maximize overall methanol production	1-D homogeneous	Novel radial flow spherical bed reactor	Graaf et al. (1988a)	Hanken (1995)	Partial differential equations were solved using orthogonal collocation numerical method and dynamic optimisation by Differential Evolution algorithm.
Manenti et al. (2011b, 2013)	To study effects of various classical assumptions on dynamic model behaviour	1-D pseudo-homogeneous	Fixed bed reactor	Graaf et al. (1988a)		Finite difference method is employed to discretise PDEs. Steady state results were set as initial conditions for dynamic model solution. Adaptive grid methodology is used to study parametric step changes
(Petera et al., 2013)	To propose new algorithm for numerical solution to full heterogeneous model of fixed bed reactor	4-D heterogeneous	Fixed bed reactor	Bussche and Froment (1996a)		Universal coupling of macro- and micro-geometries represented by two finite element meshes system.

two stage reactors with boiling water circulated as the cooling media in both stages. They performed a steady state optimisation of temperature profiles of the two reactors separately using multi-objective genetic algorithm (Kordabadi and Jahanmiri, 2007). The results indicated an increase in the production rate.

Elkamel et al. (2009) developed a superstructure model based on Lurgi type reactor to devise network configuration for multiple reactors. The model was validated against the real plant data and found to be more efficient and less cost intensive when a double reactor parallel system (2 × 2) is used. Methanol yield in (2 × 2) configuration was 37.5% compared to 29.2% of single reactor.

Manenti et al. (2011a) made a comparative study of three different types of models and compared their results. Models included classical pseudo-homogeneous, modified pseudo-homogeneous and heterogeneous. The results suggested that the assumption of constant amount of moles (considered in classical pseudo-homogeneous models) be discarded as it may lead to a 10% error in the final methanol fraction. Additionally, heterogeneous model gives results similar to the modified pseudo-homogeneous model which is a key to avoid complexities in solving PDEs.

Riaz and Zahedi (2012) proposed integration of methane steam reformer and methanol reactor. Dynamic study on the configuration showed marked increase in production levels, as high as 10% in addition to savings on capital investments. Abrol and Hilton (2012) developed mathematical model for methanol reactor–separator loop performance for varying flow of syngas and the dynamic model was used to design linear model predictive controller for regulatory control.

3.3.2. *Membrane reactors*

In order to overcome equilibrium limitations (as they impede higher yields in methanol synthesis reactions), in situ removal of products by applying selective membrane separation was proposed by Struis et al. (1996). They employed per-fluorinated cation exchange material, Nafion-DuPont, for use as vapour permeation membrane at/up to 200 °C. In their membrane model (Struis and Stucki, 2001) the same results were reproduced, highlighting the limitation of low gas hourly space velocity.

Rahimpour and Ghader (2003) suggested a Palladium (Pd) base membrane reactor for improving H_2/CO_2 ratio inside the reactor. The model suggests a shell and tube reactor with pure hydrogen on the shell side and thin tubes of Pd. The methanol mole fraction seems to have increased with the decrease in the tube thickness and feed flow rate and higher hydrogen content and pressure. Rahimpour and Lotfinejad (2008c) studied the use of Palladium–Silver (Pd–Ag) membrane reactor in a two-stage reactor configuration. The selectivity of Pd for H_2 takes reaction in the forward direction by improving the stoichiometric number as it lets H_2 penetrate through the reactor. Improving on and utilising the benefits of Lurgi's latest two stage methanol synthesis reactor, Rahimpour et al. (2011) introduced their perm-selective membrane reactor as second of the two-stage reactor system. Effects of co- and counter-current configuration on CO removal rate, catalyst activity and hydrogen permeation rate were also investigated.

Gallucci and Basile (2007) modelled a traditional methanol reactor and used the model for behavioural prediction of ceramic membrane reactor. Zeolite membrane was chosen based on its separation properties as they only allow vapours to permeate. The theoretical study needed experimental backup or validation especially when kinetics were considered to be identical to that of traditional reactor and the assumption of zeolite not permitting gases to permeate through. In the experimental study, Gallucci et al. (2004) demonstrated the possibility of obtaining increased methanol selectivity and yield in zeolite methanol reactor compared to traditional reactor.

Parvasi et al. (2009) modelled a novel methanol synthesis loop and optimised the model using differential evolution technique. The recycle gas stream was passed through the Pd–Ag membrane reactor before mixing with the makeup stream of SG. The model was validated against plant operational data and conventional methanol reactor model; 40% increase in the methanol yield was observed during the same time period. The catalyst activity was also investigated amid concentration levels of CO and CO_2 (Parvasi et al., 2008).

Farsi and Jahanmiri (2011a) introduced Pd/Ag and alumina–silica composite membrane layers for concurrent permeation of hydrogen and removal of water vapours from the reaction zone, respectively. Compared to conventional industrial reactor, this novel configuration reported 10.02% improved methanol yield.

Packed bed membrane reactor configuration is the most studied reactor type but with the production of thin and highly permeable membranes, the mass transfer limitations make this reactor unsuitable for commercialisation. Fluidised bed and/or micro-structured reactor configurations are deemed suitable as mass transfer limitations within the catalysts bed are circumvented and the membrane area required is thus minimised (Gallucci et al., 2013).

3.3.3. *Fluidized bed reactors*

The use of fluidized bed reactors has been studied widely mainly due to their advantages such as enhanced conversion, less pressure drop, elimination of diffusion limitations, good heat transfer capability and a more compact design (Abashar, 2004). Rahimpour and Alizadehhesari (2008) introduced fluidized bed concept in gas cooled reactor. Tabiś (2001) examined the idea of providing external cooling media in fluidized bed reactors. The external heat exchanger system shows promising effects on the methanol production rate. Rahimpour et al. (2010a, b) then combined the benefits of fluidized bed reactor and two-stage Pd–Ag membrane reactor. The simulation results depict a considerable increase in methanol production rate by lessening catalyst deactivation of which thermal sintering is considered as major cause.

3.3.4. *Thermally coupled reactors*

Exothermic and endothermic reactions can be coupled in a number of arrangements, which may be broadly classified as recuperative coupling, regenerative coupling and direct coupling (Ramaswamy et al., 2008). The recuperative mode of coupling keeps exothermic and endothermic reactions spatially segregated, and heat transfer takes place across the walls. A common example is a counter-current or co-current heat exchanger reactor. In regenerative mode of coupling, e.g. reverse flow reactors, the two reactions are carried out alternatively on the same catalyst bed. The endothermic reaction utilises the heat stored during the previous half cycle. Directly coupled adiabatic reactors involve simultaneous or sequential occurrence of both exothermic and endothermic reactions in the same reactor space subject to a direct heat transfer within the reacting mixture. The major concern in direct and regenerative coupling is that the catalyst bed should favour both reactions and is not deactivated or sintered by the exothermic reaction. Fig. 7 gives pictorial representation of aforementioned coupled reactors.

Thermally coupled reactors are of considerable interest (Kolios et al., 2002) to modern scientific world and various combinations are being tried. Khademi et al. (2009) modelled and simulated a heat exchange reactor consisting of two fixed beds utilizing the exothermic heat of methanol reaction for production of benzene from cyclohexane across the wall. Good agreement of results against existing conventional reactor models paved way for start-up and transient response analysis of the system (Khademi et al.,

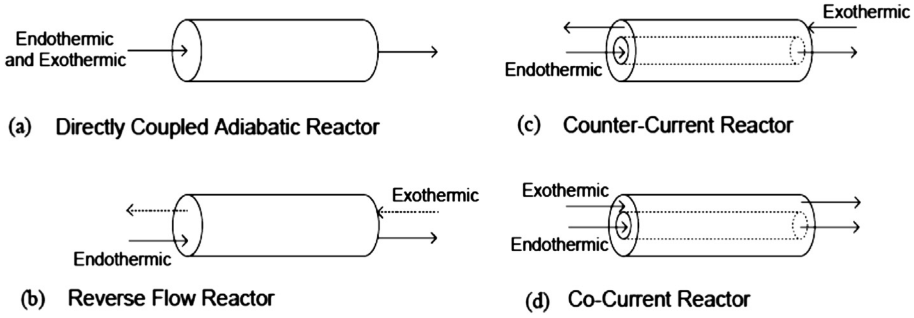

Fig. 7. Schematic of various reactor configurations for coupling exothermic and endothermic reactions (Ramaswamy et al., 2006).

2011). Specialised process control system is required to avoid glitches during the normal operation of the plant or in case of a step change in inlet conditions. Mirvakili et al. (2012) proposed optimal thermally coupled dual methanol reactor using cyclohexane and hydrogen looping approach. Dehydrogenations of cyclohexane and methanol synthesis are thermally coupled in first reactor while benzene hydrogenation to form cyclohexane is carried out in the second reactor. The simulation results show better temperature control inside the reactor.

3.3.5. Ring network/simulated moving bed

The concept of using multiple reactor(s) in a closed and open loop has not attracted many researchers. The idea of ring reactor network or simulated moving bed provides an opportunity to exploit thermal storage capability of catalyst and help optimise temperature distribution (Fissore et al., 2004a). The effect of operating variables like switching time, fluid flow rates and temperature profile on methanol yield have been studied (Mancusi et al., 2010). Initial simulation results indicate possibility of obtaining higher conversion and selectivity for methanol synthesis but this may be balanced out by the complex operation and control strategies of the system (Velardi et al., 2004). A detailed numerical model was developed by Fissore et al. (2004b) which was used to train artificial neural network for a model predictive control scheme in order to maximise methanol yield and to fulfil process constraints.

A comparison based on experiments, backed by simulations, of reverse flow, internal recirculation and loop reactors was made by Sheintuch and Nekhamkina (2004). Although, inner–outer internal recycle reactor is technically simple but it may operate better at low flow rates than reverse flow reactor. At high flow rates, the conclusion is reversed.

Bussche and Froment (1996b) came up with star configuration as a solution to major disadvantage of reverse flow scheme, i.e., the non-consistent exit stream concentration upon reversal of flow. Three reactors in a star formation are operated in a cycle comprising of three steps Inlet, Blowout and Exit (see Fig. 8). The flow direction of the reactor in 2nd step is changed by introducing fraction of the effluent from the 3rd step reactor in the reverse direction to 2nd step reactor, resultantly pushing the unconverted feed over the heated catalyst bed to react. To cater heat accumulation, a heat exchanger can be introduced at the star node to generate medium pressure steam. The configuration showed an increased methanol conversion but the operation becomes quite tedious and requires highly efficient control mechanism.

Zahn et al. (2010) proposed several adiabatic fixed beds in series as an alternative to conventional fixed bed reactor. Dynamic model for the periodic operation of reactor network was studied with true counter current of the phases involved. Authors claim to have achieved shorter computation time with accuracy for switching time and inlet temperature as compared to simulated moving bed reactor. Altimari and Mancusi (2013) introduced proportional feedback controller to manipulate switching time so as to control reaction front velocity and prevent transition to low conversion.

3.3.6. Slurry reactors

The ideology of in situ removal/separation of products to overcome thermodynamic limitations led to liquid phase methanol process. Cybulski (1994) reviewed the liquid phase methanol synthesis processes covering catalysts, kinetics and modelling. Öztürk et al. (1988) and Graaf and Beenackers (1996) compared the two-phase and three-phase processes. Wang et al. (2007) have listed some of the types of slurry reactors which include bubble column, internal-loop airlift reactor, external-loop airlift reactor, and spherical reactor, as shown in Fig. 9. The airlift reactors comprise of risers and down comers to allow channel flow to liquid solid slurry phase. The spherical reactor has higher mechanical resistance to pressure than the cylindrical column and, thus, decreases the wall thickness and reactor cost (Wang et al., 2007).

Earlier Graaf et al. (1988b) studied the kinetics of three-phase methanol synthesis followed by similar contributions by Šetinc and Levec (1999). In their report, Brown et al. (2000) described the commercial scale demonstration of liquid phase methanol process. Syngas with CO concentrations as high as 50% was tested without any adverse effect on activity of the catalyst. Liquid inside the reactor acts as a buffer to sharp transient operations. Tjandra et al. (1993) employed a trickle bed reactor for conversion of syngas with low H_2/CO ratio.

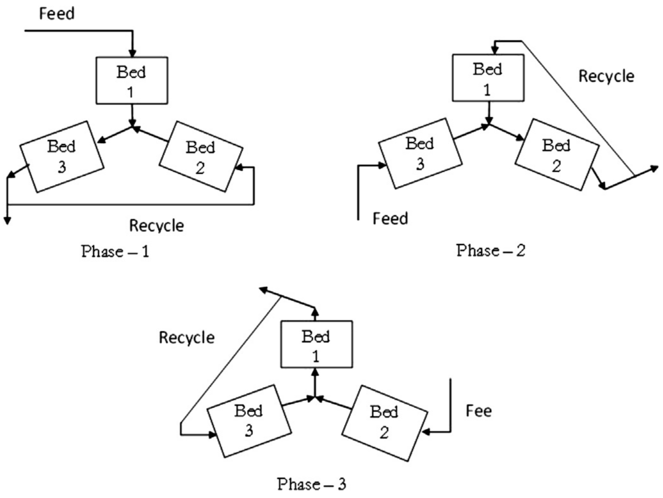

Fig. 8. Basic flow scheme for STAR reactor configuration (Bussche and Froment, 1996b).

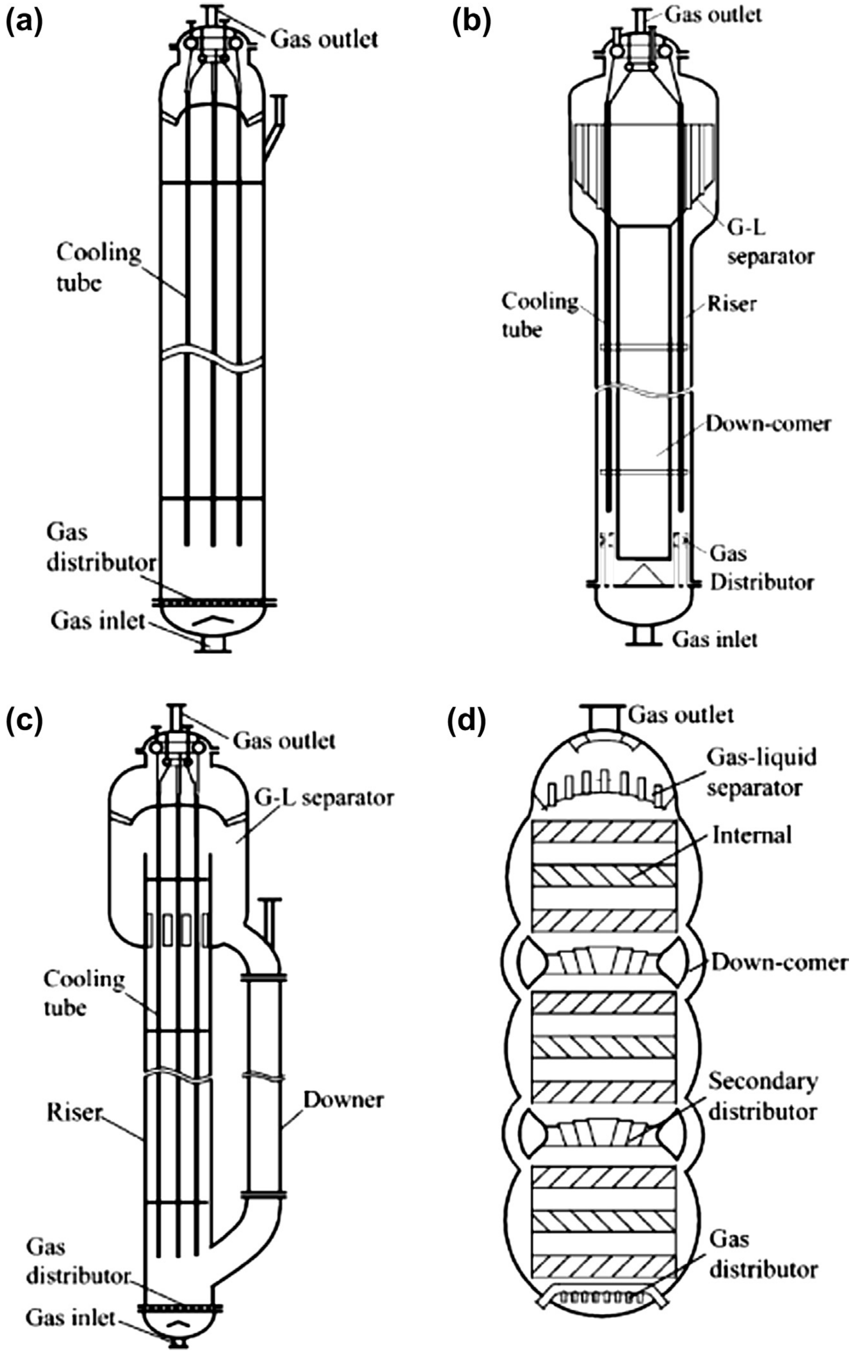

Fig. 9. Types of slurry reactors, (a) Bubble column, (b) Internal-loop shift reactor, (c) External-loop airlift reactor, (d) Spherical reactor (Wang et al., 2007).

Šetinc and Levec (2001) developed dynamic model for liquid phase methanol synthesis in a well mixed slurry reactor. Langmuir–Hinshelwood type kinetic model was used while except equilibrium adsorption constants for water and methanol, all kinetic, transport and adsorption parameters were determined experimentally. Step changes in reactor feed composition within temperature range of 200–240 °C and pressure between 34 and 41 bar highlighted the important role of water in methanol synthesis as well as proportionality of CO_2 concentration and methanol production. Wang et al. (2005) compared the performance of trickle bed and slurry reactor for methanol synthesis. The combination of orthogonal collocation and quasi-linearization was used to solve the trickle bed reactor model. Models predictions indicate that the trickle bed reactor seems more promising than slurry reactor.

Simple construction, effective heat transfer, online catalyst addition and withdrawal and scale-up for higher production rates are some of the advantages of slurry reactors. However, at the same time gas–liquid mass transfer limitations in a three-phase slurry system, hydrodynamics, liquid–solid separation and design of reactors are some of the bottlenecks demanding more research work in this area.

4. Optimisation

Optimisation strategies for avoiding the reactor catalyst deactivation have been discussed by many authors. Ogunye and Ray (1971) studied optimal control of adiabatic and isothermal reactors, optimal catalyst distribution along the reactor and feed distribution between multiple reactor beds. Elnashaie and Abdel-Hakim (1988) used a heterogeneous model to calculate optimal feed temperature of an adiabatic reactor based on both interphase and intra-particle mass and heat transfer resistances. The importance of methanol synthesis has encouraged numerous researches to optimise different reactor systems in the presence of long-term catalyst deactivation.

Larsson et al. (1999) studied unconstrained optimisation of an isothermal methanol reactor at steady state. The reactor was modelled as a series of isothermal continuously stirred tank reactors, with a kinetic model from Bussche and Froment (1996a). Løvik et al. (1998) studied dynamic optimisation of methanol reactor using (gPROMS, 2012) for optimal control of reactor's coolant temperature and recycle ratio. Objective was to maximise reactor performance eyeing long-term catalyst deactivation. Jahanmiri and Eslamloueyan (2002) investigated the optimal temperature profile in a steady state methanol reactor. They used control variable parameterization to determine the optimal temperature profile inside a methanol reactor. Kordabadi and Jahanmiri (2005) attempted to find the optimal temperature of a methanol reactor using a genetic algorithm. They also investigated the optimal division of a bed into two sections as two reactors. Their work focused on combining steady state and multi-objective optimisation techniques to estimate optimal conditions (Kordabadi and Jahanmiri, 2007).

Operating temperature and inlet feed rate are commonly employed variables for curbing deactivation problem in methanol synthesis reactor. As a side effect, increase in operating temperature accelerates deactivation and consequent decrease in feed rate compromises methanol production. Zahedi et al. (2007a, b) have reviewed some earlier works in this dynamic optimisation problem and also considered two practically important industrial parameters inlet hydrogen concentration and coolant water temperature. Both were simultaneously optimised using control vector parameterization strategy in a heterogeneous model (for better accuracy) under operating constraints. The optimal values of these parameters showed an increase in production rate by 1.4%, when compared with an industrial data. Parvasi et al. (2008) investigated optimal inlet temperature for methanol reactor system.

Parvasi et al. (2009) developed a dynamic model and optimised for methanol production rate using differential evolution technique. Recently, Farsi and Jahanmiri (2011b) determined optimal operating conditions for a catalytic dual-type membrane reactor. For this purpose, a heterogeneous steady state model was developed. Kralj and Glavič (2009) applied nonlinear programming optimisation techniques to methanol plant by altering flow rate of H_2 and steam. The model was aimed at heat integration and electricity cogeneration and modifying the separation and reaction systems. Rahimpour et al. (2009) performed dynamic simulation of spherical multi-stage reactors in the presence of long-term catalyst deactivation. The radial flow reactor was optimised using differential evolution algorithm for improvement in reactor performance at low-pressure drop.

Once a chemical plant is operational, engineers and managers are required to maximise production and minimise cost. Profits increase with the increase in yields of valuable products, decrease in energy consumption and longer operational periods without shutdown. As mentioned earlier, the performance of a reaction system is adversely affected by deactivation of the catalyst as can be observed from the decrease in methanol production rate (Fig. 10).

Shahrokhi and Baghmisheh (2005) devised an online optimisation strategy to maximise methanol yield while at the same time tune PID controller for hot spot temperature protection. The steady state model considers process disturbances but does not account for transient nature amid catalyst deactivation. Mohd Fuad et al. (2012) proposed an estimation–optimisation strategy wherein reactor's coolant temperature is constantly updated as the catalyst deactivates with feedback from the process measurements. The results show potential to maximise total methanol production by maximal utilisation of catalyst throughout its service life.

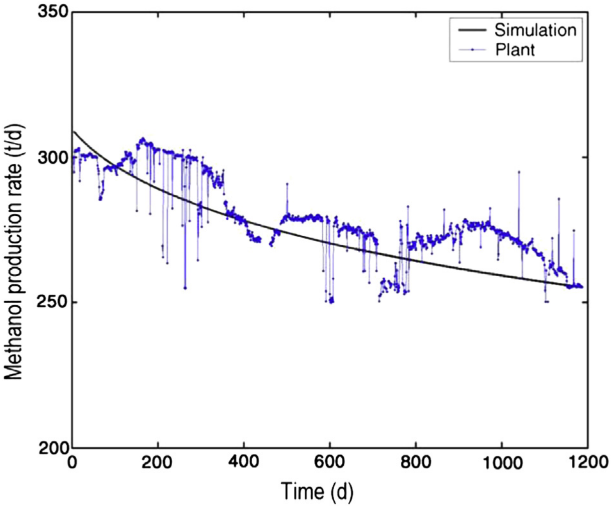

Fig. 10. Simulation result and plant data for methanol production rate during catalyst service life (Rezaie et al., 2005).

5. Life cycle assessment

Life cycle analysis (LCA) of a product refers to the impacts made by the product(s) on environment at each and every stage of the production cycle, from extraction of raw materials to waste disposal. LCA is carried out in four steps (Varanda et al., 2011):

- Purpose and Scope
- Inventory
- Impact Assessment
- Analysis and Improvement

Referring to Fig. 1, the share of methanol as blending component in gasoline is projected to increase from current value of 11 to 16%. Now this has dual impact as there will be 5% less utilisation of fossil fuel and on the other hand CO_2 shall be utilised in the production of methanol. Harkin et al. (2012) suggested installing carbon capture sequestration units next to power plants. In this context, methanol can serve as an excellent route to help lower carbon emissions. A complete LCA of methanol can help in projecting the complete picture. Mignard et al. (2003) proposed to utilize CO_2 emitted from fossil fuelled power stations and hydrogen from electrolysis of water using renewable or nuclear energy source to produce methanol. Authors carried out a preliminary economic analysis based on the available renewable energy during off-peak times in UK. Soltanieh et al. (2012) proposed similar scheme using wind as renewable energy source for electrolytic hydrogen. The major challenges in all these proposals are continuously producing of huge amount of carbon-free hydrogen (Pontzen et al., 2011) and for more recent and extended overview see (Van-Dal and Bouallou, 2012).

For the quantification of the LCA-based environmental impacts selected footprints are used (Čuček et al., 2012a). Beside Carbon Footprint other footprints like Nitrogen Footprint should be considered (Čuček et al., 2012b). The footprints can be implemented in the Environmental Performance Strategy Map, which offers an integrated LCA approach to support the strategic decision making process (De Benedetto and Klemeš, 2009).

6. Conclusion

Competition with the existing and far established energy sources is imperative and inevitable for all alternative energy sources. Over the years, improvements in the practical efficiencies have been achieved by a combination of chemical engineering and catalyst development. Further development of methanol synthesis technology has the potential of reducing overall plant cost. SG routes are highly efficient, but capital intensive because they involve exchange of energy in the reformers and heat recovery units. Economic swing is in favour of methanol riding the fact that rising oil prices are being forecast to be robust into the long-term. At the same time, methanol is expected to increase its consumption in blending with gasoline fuel. Modelling of different types of reactors and their combinatorial configurations has been studied in recent past to economise the scale of methanol production. From traditional packed bed reactors to three-phase slurry reactors and to direct conversion of natural gas to methanol have been modelled. In this regard, fluidized bed reactors, membrane reactors and thermally coupled reactors appear to show more promise and have potential for industrial testing in the near future.

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Nomenclature

Roman letters

a	activity of the catalyst
a_i	activity of the components (as used in Table 2)
c	concentration
D	dispersion diffusivity
E	activation energy
g	concentrations of reaction intermediates
ΔH_r	heat of reaction
k	rate constant
K	diffusion constant
MSR	Methane Steam Reforming
n	sintering order
NG	natural gas
P	pressure
r	rate of reaction
S	active metal surface area
SG	synthesis gas
SN	stoichiometric number
T	temperature
W	Watt (unit of electrical power)
z	reactor length

Greek letters

η	effectiveness factor
μ	viscosity

Superscripts

s	steady state
$\underline{o}$	for stagnant component
eq	at equilibrium

Subscripts

0	initial
act	actual
d	deactivation
eq	equivalent
K	Knudson (diffusivity)
r	reaction
R	reference
s	catalyst surface sintering
sat	saturated

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