

Review of methane cracking over carbon-based catalyst for energy and fuels

Original

Review of methane cracking over carbon-based catalyst for energy and fuels / Mirkarimi, S. M. R.; Bensaid, S.; Negro, V.; Chiaramonti, D.. - In: RENEWABLE & SUSTAINABLE ENERGY REVIEWS. - ISSN 1364-0321. - 187:(2023), pp. 1-16. [10.1016/j.rser.2023.113747]

Availability:

This version is available at: 11583/2983583 since: 2023-11-03T14:03:52Z

Publisher:

Elsevier

Published

DOI:10.1016/j.rser.2023.113747

Terms of use:

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright

(Article begins on next page)



Review of methane cracking over carbon-based catalyst for energy and fuels

S.M.R. Mirkarimi^a, S. Bensaid^a, V. Negro^b, D. Chiaramonti^{b,*}

^a Politecnico di Torino, DISAT, Torino, Italy

^b Politecnico di Torino, DENERG, Torino, Italy

ARTICLE INFO

Keywords:

Hydrogen
Catalytic methane decomposition
Carbon-based catalyst
Methane cracking
Metal-carbon catalyst

ABSTRACT

Catalytic decomposition of methane is today considered as a pathway to hydrogen production that - unlike the other well-known methods - can convert methane into hydrogen without generating CO_x emission, but rather delivering solid Carbon, a storable and useable product which, in case of biomethane cracking, generates biogenic Carbon and a Carbon Negative route (Negative Emission Technology). Although mostly metallic catalysts have been used for this purpose, due to the rapid deactivation of this type of catalyst and the challenges of their regeneration, methane decomposition over carbon materials attracted some attention during recent years. This work provides a review of the recent studies performed on hydrogen production through methane cracking over carbon-based catalyst. The impact of operating parameters such as reaction temperature, pressure, feedstock purity, space velocity as well as the catalyst characteristics including particle size, surface area, pore volume, oxygenated compounds, and ash content on methane decomposition has been widely discussed in this review. Based on the literatures, operating temperature more than 800 °C and space velocity less than 1 L/g.h for pure methane are required to provide methane conversion higher than 50%. Also, reducing the concentration of methane in feedstock with inert gases as well as using carbon-based catalysts with lower particle size, higher surface area, more mesopores and oxygenated compounds can reach to an enhancement in methane conversion. Also, investigation on impact of ash content shows loading metals such as Fe, Ni, Ca, and Pd metals over carbonaceous materials improve their catalytic activities.

1. Introduction

Continuous growth of global population and the climate change impacts also connected to fossil fuel use lead to an increased demand for sustainable and efficient sources of energy. Recently, the production of hydrogen as a highly efficient and clean energy vector is attracting more attention. Based on the demand for a clean energy vector, it is anticipated hydrogen production reach to 122.5 M tons in 2024 [1]. The amount of energy produced during hydrogen combustion is higher than that released by any other fuel on a mass basis, with a low heating value 2.4, 2.8 and 4 times higher than that of methane, gasoline and coal, respectively [2]. Steam methane reforming (SMR) is the most used technology for hydrogen production: almost 50% of global hydrogen is obtained through this process [3]. Partial oxidation of methane (POM) and dry reforming of methane (DRM) are the other two process routes employed to produce hydrogen at the industrial scale [4,5]. As shown in Table 1, the CO produced as a by-product in these conventional

processes gives rise to the simultaneous production of CO₂ through the water-gas shift reaction. Actually, the only alternative technology which can produce hydrogen from methane without CO₂ emission is methane pyrolysis. This is the single-step process of methane conversion into hydrogen and carbon (Table 1). Although comparing the reactions of SMR, POM, and DRM with methane pyrolysis shows the theoretical hydrogen produced per given amount of methane is less through methane pyrolysis (H₂/CH₄ = 2 for methane pyrolysis process whereas this ratio is more than 2 for other processes by consideration of H₂ production also through Water Gas Shift process), the challenges for hydrogen separation from CO and CO₂ as well as the energy required for CO₂ sequestration lead to a reduction in the total energy amount which is obtained from hydrogen produced in these two pathways. Also, due to Carbon prices already applied to CO₂ emissions from energy-intensive industries (e.g. EU Emission Trading Schemes), the methane pyrolysis process could thus be very attractive compared to a fully mature process like SMR [6,7].

Comparing different methods of hydrogen production shows

* Corresponding author.

E-mail address: david.chiaramonti@polito.it (D. Chiaramonti).

<https://doi.org/10.1016/j.rser.2023.113747>

Received 3 March 2023; Received in revised form 8 September 2023; Accepted 10 September 2023

Available online 20 September 2023

1364-0321/© 2023 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

Abbreviation

CMD	Catalytic methane decomposition
DRM	Dry reforming of methane
POM	Partial oxidation of methane
SMR	Steam methane reforming
VHSV	Volume hourly space velocity

Table 1
Main methods of methane, water and CO conversion into hydrogen.

Process	Reaction	Enthalpy [kJ/mol]
SMR - Steam methane reforming	$\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$	206
POM - Partial oxidation of methane	$\text{CH}_4 + 0.5\text{O}_2 \rightarrow \text{CO} + 2\text{H}_2$	-23
DRM - Dry reforming of methane	$\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$	247
Methane pyrolysis	$\text{CH}_4 \rightarrow \text{C(S)} + 2\text{H}_2$	75
Water gas shift	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$	-41
Water electrolysis	$\text{H}_2\text{O} \rightarrow \text{H}_2 + 0.5\text{O}_2$	285

Table 2
GHG emissions and hydrogen production cost production of natural gas decomposition and other conventional methods of hydrogen production [8–10].

Process	GHG Emissions [kg CO ₂ -eq./kg H ₂]	Hydrogen Production Cost
SMR	11.35	1.22 [\$/kg H ₂]
SMR with 85% Carbon Capture	6.66	2.36 [\$/kg H ₂]
Electrolysis of Water	1–5	3.7 [€/kg H ₂]
Natural gas decomposition	4.89	2.12 [\$/kg H ₂]

Table 3
Opportunities and challenges of using SMR, DRM, POM, and CMD processes for hydrogen production [5,16–19]

Process	Advantages	Disadvantages
SMR	<ul style="list-style-type: none"> • High process efficiency • Low operational and production cost • Higher H₂/CO ratio compared to the other technologies • Fully mature system 	<ul style="list-style-type: none"> • High CO_x emission • Energy intensive process • High capital investment
POM	<ul style="list-style-type: none"> • High conversion rates • High selectivity • Very short residence time 	<ul style="list-style-type: none"> • Operation control is difficult • Requiring pure O₂
DRM	<ul style="list-style-type: none"> • CO₂ conversion offers valuable environmental benefits • Mild reaction conditions 	<ul style="list-style-type: none"> • Carbon deposition problem • Influenced by reverse water gas shift reaction • Limited commercial experience
Methane pyrolysis	<ul style="list-style-type: none"> • One step process • Production of pure H₂ • Zero CO_x emission • Production of valuable byproduct (graphitic-carbon) 	<ul style="list-style-type: none"> • Still under development, at different stages depending on the considered technical solution • Rapid deactivation of metallic catalyst • Low catalytic activity of carbon-based catalyst • Technical challenges of using plasma

although the least GHG is emitted through electrolysis of water, the cost of hydrogen production through this technology is much higher than natural gas decomposition, SMR and even SMR with 85% carbon capture. Hydrogen production through natural gas decomposition has the

minimum GHG emission after process of water electrolysis and the hydrogen production cost by this method is less than water electrolysis and SMR with 85% Carbon Capture. Only the cost of hydrogen production from SMR is less than natural gas decomposition, but it should be noticed that the kg CO₂-eq. which emitted per each kg H₂, is more than twice the natural gas pyrolysis [8–10] (see Table 2).

Through utilization of carbon in different industries, hydrogen production from methane pyrolysis is economically competitive even compared with conventional technologies [11–14]. Prices for carbon products range from 400 to 2000 €/t for carbon black itself and significantly higher prices of >1,000,000 €/t can be achieved for high grade special carbon products [15]. Methane pyrolysis is even significantly more economical than electrochemical-based processes using commercial renewable power sources, for low-CO₂ hydrogen production [7]. Table 3 shows a brief report about the advantages and challenges of different technologies for hydrogen production from methane including SMR, DRM, POM, and methane pyrolysis.

Based on the literature, methane pyrolysis can be divided into three categories: Thermal decomposition, Plasma decomposition and Catalytic decomposition [19]. Methane cracking in presence of a catalyst normally occurs in a temperature range of 700–950 °C, while a temperature of around 1200 °C is required for the non-catalytic methane decomposition [20]. Methane decomposition by plasma requires high local energy densities and temperatures range of 700–5500 °C [21]. Large gas volume flows are usually recirculated to stabilize the plasma [19]. Under European supply chain conditions (10.1 and 17.0 g CO₂-eq./MJ [22]), the plasma methane decomposition using electricity from renewables (RE) produces hydrogen with 67–77% lower GHG emissions than steam methane reforming and this is also 55% lower under global condition [23]. One of the advantages of plasma processes is low inertia and the fast start up of the system that let them to be combined with a fluctuating electricity supply from renewable energy sources such as wind power or solar radiation [23]. High methane conversion (more than 80%) has been claimed through thermal plasma processes [21]. Rapid and noncontact heating is another benefit of this technology. However, electrode wear, cooling, and carbon deposits are among the greatest technical challenges of using plasma for methane decomposition [19]. Kvaerner and Monolith Materials technologies are two of the most prominent examples of using plasma, however in both of these technologies, hydrogen is just a by-product [23].

Catalytic methane decomposition (CMD) is another technique for pyrolysis of methane and hydrogen production. The two main groups of catalysts utilized in the CMD process are metallic catalysts and carbon-based catalysts. The methane pyrolysis has been extensively studied over different metal (Ni, Co, Fe) and carbon catalysts, however, from an industrial point of view, only the use of iron and carbon catalysts is viable due to their nontoxicity [6,24]. In a simulation study [25], two scenarios of catalytic methane pyrolysis over the iron-based catalyst with H₂ combustion (CMD-H2) and CH₄ combustion (CMD-CH4), were compared to the Steam Methane Reforming with carbon capture and sequestration (SMR-CCS). It was claimed for large-scale hydrogen production (216 tons/day), the cost of hydrogen production, without considering carbon sales, was estimated to be < 3.25 \$/kg which was comparable with hydrogen production cost via SMR (almost 2.2 \$/kg). This evaluation was carried out based on a natural gas price of 7 \$/MMBtu and a conservative catalyst cost of 8 \$/kg. In another simulation research, a techno-economic analysis was carried out for a hydrogen-burning power plant with an onsite hydrogen production unit based on methane catalytic decomposition [26]. It was reported that CO₂ emission was reduced by 80.2% compared to direct power generation from natural gas through using hydrogen-burning power plant, however, it costs a 44% reduction in power due to the lower heating value of H₂ compared to CH₄. High catalyst price was reported as one of the obstacles to the profitability of the power plant working by hydrogen produced from CMD. Although metallic catalysts show higher catalytic activity compared to the carbon-based catalyst, their rapid deactivation

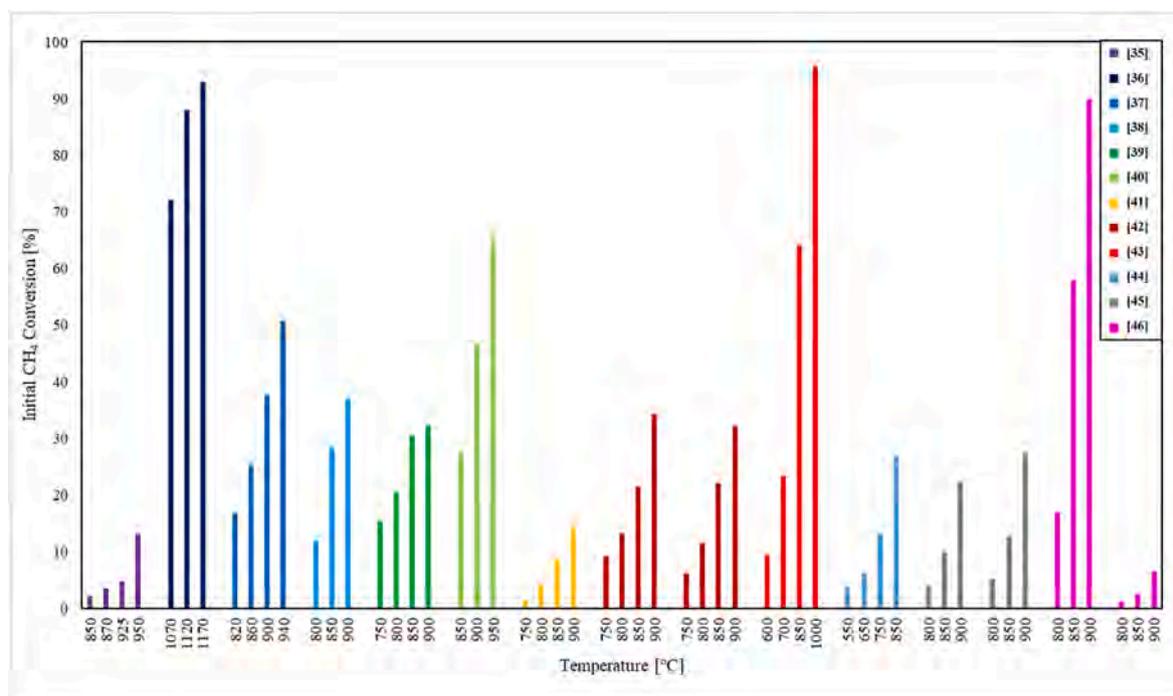


Fig. 1. Impact of temperature on initial methane conversion in presence of carbon-based catalysts [59–70].

due to carbon deposition is their main drawback. Also, the regeneration of metal-based catalysts and separating carbon materials are the other challenges of using metallic catalysts. Although carbon-based catalysts are less effective than metallic ones, their advantages could outweigh this limitation. The catalysts produced from carbon materials are cheaper than the metallic ones, also they are more resistant to impurities and high temperatures. Thus, unlike metallic catalysts which produce CO₂ during regeneration, using carbon materials as the catalyst does not cause CO₂ emissions. Furthermore, the carbon of methane would be deposited on the carbon-based catalyst and a marketable byproduct of carbon would be formed [13].

Carbonaceous catalysts are divided into three groups based on crystallinity: highly ordered (graphite, diamond), less-ordered (glassy carbon, fullerene C60/70, fullerene soot, carbon nanotubes, and ordered mesoporous carbons), and disordered carbons (amorphous, microcrystalline, such as coal char, activated carbon, carbon black, and acetylene carbon) [27]. Disordered carbons show a dislocated arrangement of C–H bonds which causes dislocations, vacancies, low-coordination sites, atoms with free valences, discontinuities, edges, and defects, called high-energy sites. The initial activity of the carbon-based catalyst increases with rising high-energy sites. Therefore, the activity of less ordered (turbostratic) is higher than that of highly ordered carbons, but less than disordered carbons [28]. In literature, most studies concern disordered carbons, especially activated carbon and carbon black, since they offer the best catalytic performance. Various carbonaceous catalysts such as wood char [29], activated carbon [30,31], carbon black [31,32], ordered mesoporous carbon [33], graphite [34], glassy carbon [35], multi-wall nanotubes [36], acetylene black [35], soot [35], diamond powder [35], carbon nanotubes (CNT) [36] and fullerenes [35] have been investigated for CMD process: among these, activated carbon and carbon black have attracted more attention compared to the others.

A large number of studies performed on catalytic methane decomposition exist; however, few review papers have been published in this area, which mostly discussed the performance of the metallic catalysts in the CMD process. The main focus of this review is to investigate the most recent research literature on producing and using carbon-based catalysts for hydrogen production through methane cracking. In this paper, the impact of reactor configuration and operating parameters such as

temperature, pressure, feedstock purity, and space velocity as well as catalyst characteristics such as particle size, surface area, pore volume, oxygenated compounds, and ash content has been comprehensively discussed and assessed, providing the essential information to design effective solutions for methane cracking over carbon bed. This work presents the optimum operating conditions as well as the most suitable carbon-based catalysts characteristics to obtain maximum level of methane conversion through reviewing the results of 36 studies carried out on the methane pyrolysis using carbon-based catalysts.

2. Reactor configuration for catalytic methane decomposition

Maximum catalytic methane conversion is highly dependent on the reactor system configuration. The first issue regarding the reactor design is related to the material selected for the reactor. Since methane pyrolysis occurs at high temperatures (above 800 °C), selecting a proper reactor material that can be high temperature resistant and inert towards the reaction is crucial. Stainless steel, Ceramic, and Quartz are the most common materials used for CMD reactors.

Stainless steel reactors can be used for high-pressure and temperature applications [37], also due to their availability and low cost, they are the best option for the CMD process on the commercial scale [38]. However, the major concern about using stainless steel material is that iron and its alloy become catalytically activated at such a kind of high temperature [39] which can cause damage the reactor through the formation of some carbide materials [40]. Due to this issue, using stainless steels such as 310 and 353 with higher Nickel and Chromium are recommended, since at high temperature, they have better corrosion resistance compared to the common type of stainless steel 316. Quartz and ceramic are catalytically stable at higher temperatures up to 1500 °C [37], however, they are not suitable for large-scale applications.

Methane decomposition has been widely studied in both conventional and unconventional reactors. The conventional thermal reactors used for methane cracking are further categorized into three groups 1) Fixed-bed reactor, 2) Fluidized bed reactor, and 3) Molten metal reactor, based on their vessel configuration. Also, the Plasma bed reactor is one of the popular unconventional reactors used widely for the methane pyrolysis process to produce hydrogen [41,42].

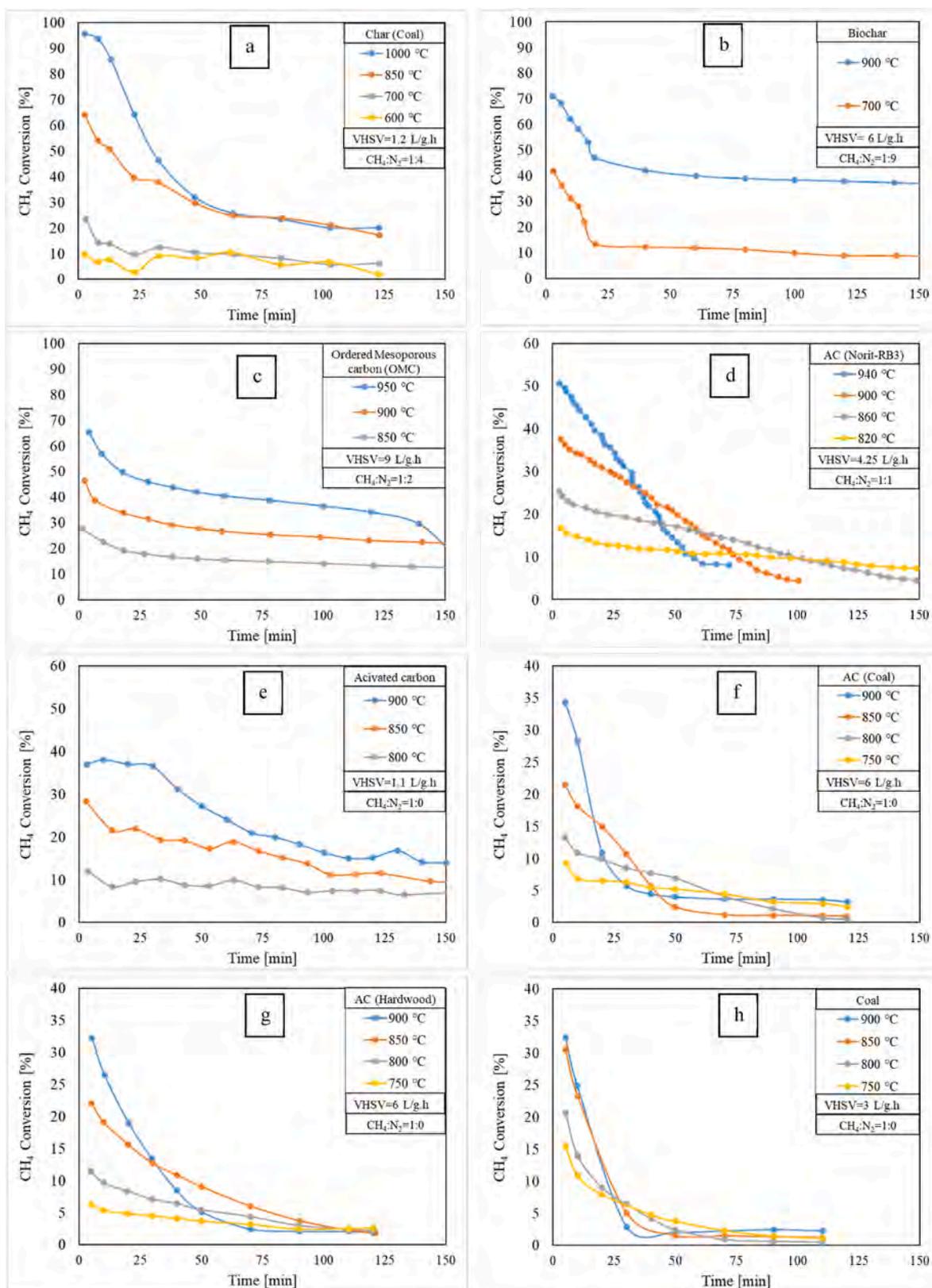


Fig. 2. Impact of temperature on methane decomposition over, (a): char coal [65], (b): biochar [71], (c): ordered mesoporous carbon [62], (d): Norit-RB3 [69], (e): activated carbon [70], (f): activated coal [64], (g): activated hardwood [64], (h): coal [61], (i): coal [67], (j): activated coal [66], (k): activated hazelnut shell [72], (l): coal [67], (m): activated coconut shell [63], (n): coal [59].

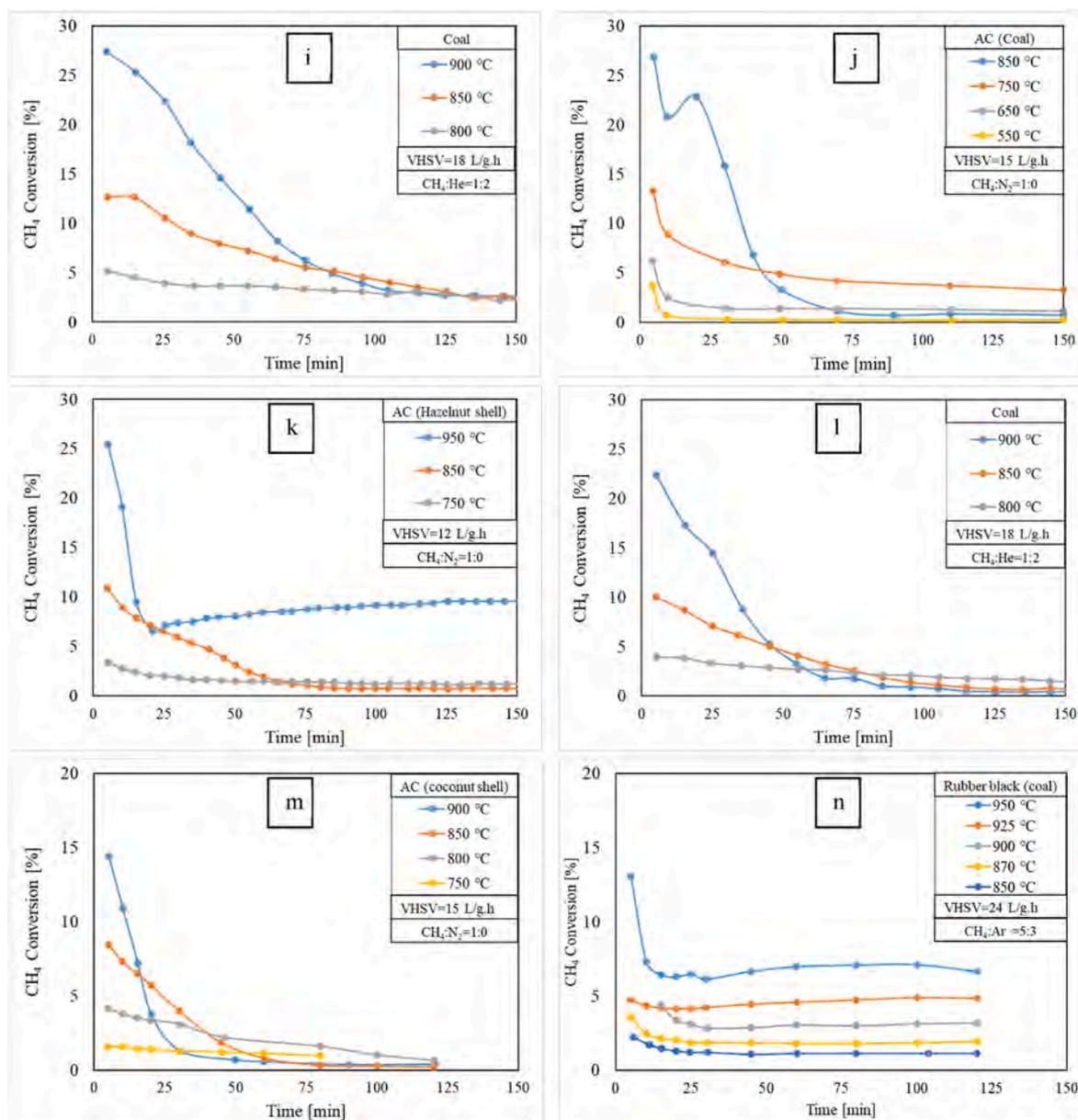


Fig. 2. (continued).

2.1. Fixed-bed reactor

Due to the simplicity of design and controlling the operating condition, the first studies regarding reactor design for catalytic methane decomposition were performed in fixed-bed reactors. These reactors are commonly used on a laboratory scale to investigate the impact of operating parameters as well as catalyst characteristics on hydrogen production and carbon nanomaterials generation. A vertical fixed-bed with the catalyst bed loaded in the heating zone of the reactor is the most common orientation of the fixed-bed reactor for methane cracking [43,44]. Horizontal fixed-bed reactors are also reported for CMD in some literature [45,46]. However, fixing the catalyst in a proper position inside a horizontal reactor is one of the challenges of using a fixed-bed reactor in a horizontal orientation. Although the fixed-bed reactor has flexibility in design and could be the best choice for studying the effect of different experimental parameters on methane conversion, this type of reactor cannot be used in continuous mode on commercial scale due to the mass transfer limitation occurs because of carbon formation and blockage of the active sites of the catalyst [42].

Moreover, the temperature profile is not uniform inside the fixed-bed reactor which can create a hotspot inside the reactor and damage the reactor and catalysts over time as well as influencing the performance of the catalyst and subsequent hydrogen yield [47].

2.2. Fluidized bed reactor

Since the deposited carbon and deactivated catalyst are periodically replaced with fresh catalysts in a fluidized bed system, this type of reactor can be utilized for CMD on a commercial scale for the production of hydrogen in continuous mode [48]. Furthermore, the catalyst bed behaves like a well-mixed body of fluid which improve the mass and heat transfer inside the reactor and maximizes methane cracking during the process [49]. Due to the numerous advantages of fluidized bed reactors, lots of studies have been conducted on CDM inside the fluidized bed reactors over carbon-based catalysts [47,50,51]. It can be concluded that for continues hydrogen production from the CMD process, the fluidized bed is one of the most suitable options from many aspects. However, a reduction in the overall efficiency of this type of reactor has

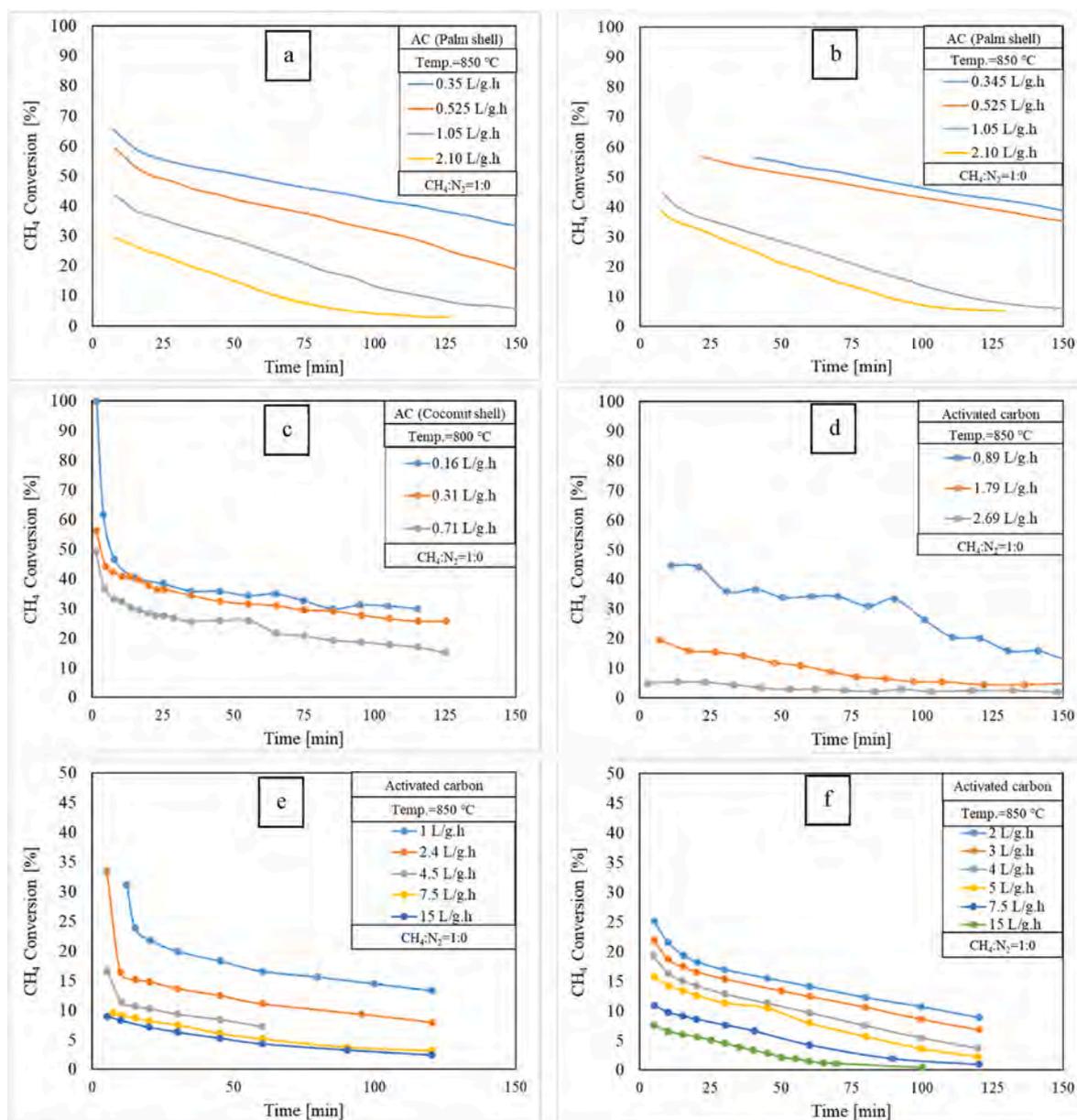


Fig. 3. Impact of space velocity on methane decomposition over (a), (b): activated palm shell [75], (c): activated coconut shell [76], (d): activated carbon [70], (e), (f): activated carbon [63].

been observed when the reactant gas bypasses through the bed unreacted, due to small particle sizes of the catalysts [52].

2.3. Molten metal reactor

Recently, extended research has been performed regarding using molten metal reactors for CMD. Carbon deposition is avoided in this type of reactor because the carbon is separated from molten metal catalysts due to the difference in density [53]. Since the main focus of this paper is on carbon-based catalysts and the basis of molten metal reactors is on using metallic catalysts which is beyond the scope of this paper, this type of reactor is not discussed in more detail.

2.4. Plasma bed reactor

Methane decomposition at very high temperatures through plasma technologies such as microwave plasma, spark plasma, and other non-thermal plasma attracts lots of attention in recent years. Primarily,

plasma reactors have two types (i) thermal and (ii) non-thermal plasma reactors. Methane decomposition through thermal plasma occurs in the absence of catalysts, so high temperature and pressure are required which means the level of energy required for thermal plasma reactor systems is higher than the conventional CDM [54]. Also, the extremely high temperatures of the reactor make it difficult for handling and maintain [42]. Non-thermal plasma reactors require lower energy input and operate at lower temperatures and pressure, thus this type of plasma reactor is more suitable for an endothermic process such as CDM [55]. Using catalysts inside the plasma bed reactor can increase conversion and allows the reactor to process higher methane flows [56]. Although plasma reactors can be an alternative to the standard catalytic beds, using this type of reactor leads to the formation of heavier hydrocarbon (mainly C2 and C3), alongside hydrogen through methane decomposition [57]. Thus, low selectivity and requiring high power input causes plasma technology cannot compete with the conventional reactor for endothermic processes like methane pyrolysis [58].

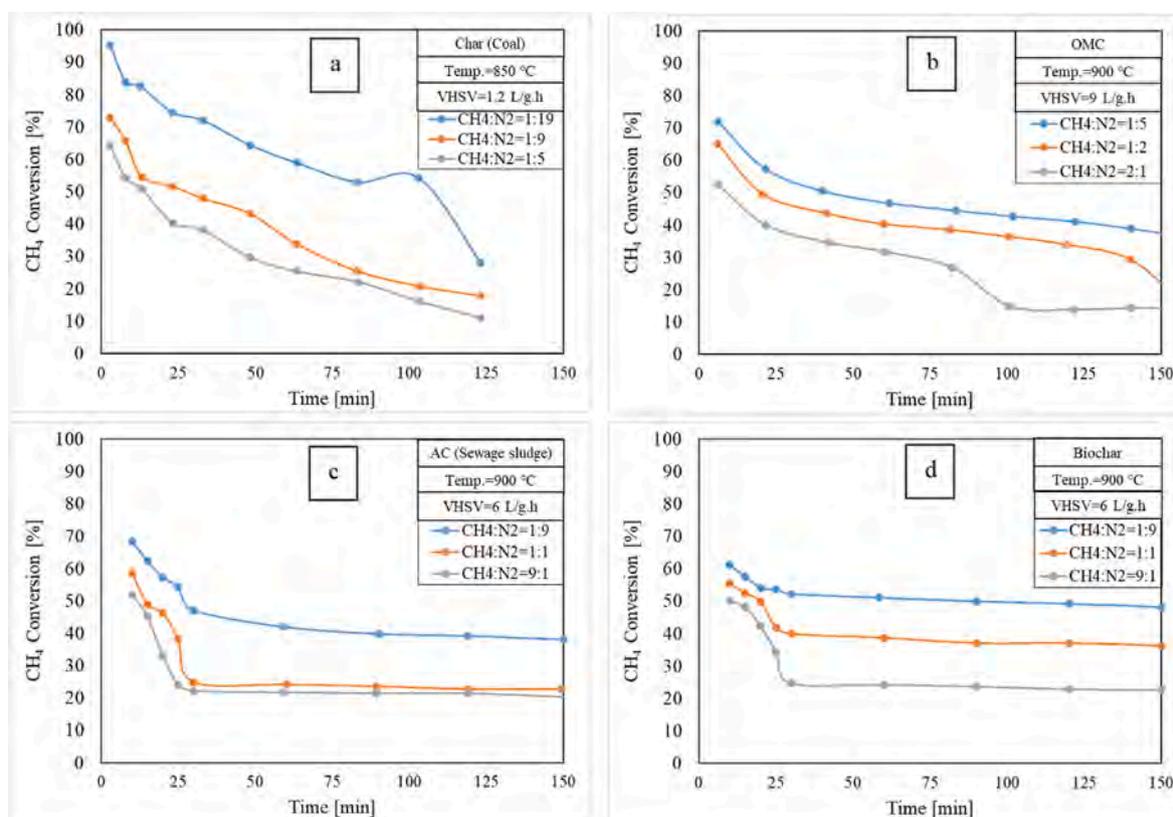


Fig. 4. Impact of feedstock purity on methane decomposition in presence of (a): char coal [65], (b): ordered mesoporous carbon [62], (c): activated char from sewage sludge, (d): bichar [71].

Table 4

Typical composition of natural gas [81].

Components	Chemical composition	Range [mol%]
Methane	CH ₄	91.10–98.79
Ethane	C ₂ H ₆	0.44–7.48
Propane	C ₃ H ₈	0.10–1.67
Butane	C ₄ H ₁₀	0.04–0.79
Heavier Hydrocarbon	C ₅ +	0.00–0.24
Carbon Dioxide	CO ₂	0.00–1.07
Nitrogen	N ₂	0.14–0.55
Hydrogen Sulphide	HF	0.00–0.00013

3. Effect of operating parameters

Conversion of methane into hydrogen through CMD could not be industrially feasible unless the process is run at optimum operating conditions. Based on literature analysis, the most common operating parameters, which have a direct impact on the hydrogen yield, have been identified as temperature, pressure, space velocity, and feedstock purity. Before explaining the impact of each parameter, it is required to mention that although all the studies reviewed for this purpose are related to the carbon-based materials, there could be a negligible error in comparing the results of different studies due to the difference in the origin material used for production carbon catalyst.

3.1. Temperature

Since CMD is an endothermic process, higher temperature leads to shift the equilibrium toward the products (hydrogen and carbon): thus, higher hydrogen yields could be obtained at higher temperature. As shown in Fig. 1, generally a temperature between 750 °C and 900 °C has been used for CMD: as said, increasing temperature leads to higher

initial methane conversion. Although most of the data reported for initial conversion is in the range of 20–30 vol% at 850 °C and 30–40 vol% at 900 °C, methane cracking with initial conversion higher than 50 vol% also has been observed at temperature range of 850–900 °C. The difference in methane conversion at a set temperature could be the result of changing the other operating parameters or using a catalyst with different characteristics.

Fig. 2 shows the impact of temperature on methane conversion during 150 min of the reaction and VHSV, which is the Volume Hourly Space Velocity which means the total flow rate at normal conditions per gram of catalyst initially loaded. As it is shown in Fig. 2, more methane is initially converted into hydrogen at higher temperature: as inevitable consequence, more carbon is deposited on the surface of catalysts that causes faster deactivation of catalyst. At high temperature, catalyst pores including a large number of active sites would rapidly block by the carbon produced through methane cracking, and thus the catalyst available surface area would be reduced very fast. On the contrary, based on literature analysis, working at temperature lower than 800 °C has generally not been recommended due to too low methane conversion (less than 20 vol%).

3.2. Pressure

Based on Le Chatelier's principle, increasing the system pressure leads to a shift in the equilibrium toward the smaller volume at a constant temperature. Since during methane decomposition the volume of gas rises, higher pressure is not favorable during this process. The impact of pressure on methane conversion has been studied by Younessi-Sinaki et al. [73] and based on their model, increasing operating pressure results in lower hydrogen production. Chen et al. [74] also modeled the methane decomposition process to evaluate the amount of hydrogen produced under vacuum conditions. Based on their analysis, the decomposition of methane at vacuum pressure with carbon separation

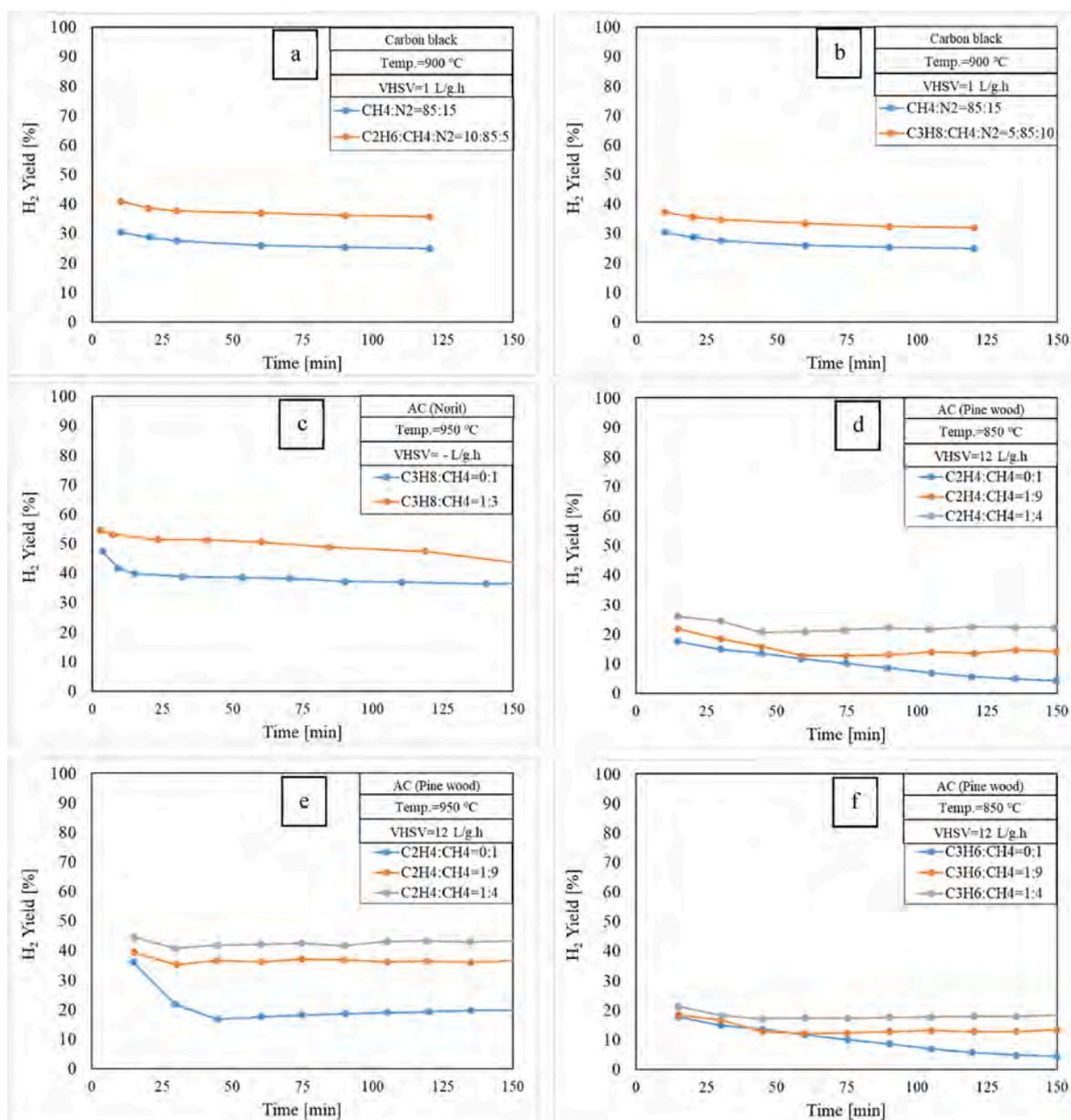


Fig. 5. Impact of minor components of natural gas on hydrogen yield and methane conversion in presence of carbon-based catalysts, (a): ethane [79], (b), (c): propane [49,79], (d), (e): ethylene [80], (f), (g): propylene [82], (h), (i): ethanol [77], (j): hydrogen sulfide [78].

promotes hydrogen yield. Although - according to the economic analysis performed in this study - the cost to produce hydrogen at vacuum pressure was somehow considered as competitive to small-scale SMR, at industrial scale working under vacuum state and handling solids is very complex and may be not economical. Therefore, most of the research in this area is conducted at atmospheric pressure.

3.3. Space velocity

Space velocity is another important operating parameter for the process: it is defined as the total flow rate at normal conditions per gram of catalyst initially loaded. Based on this definition, the effect of this parameter on process performances could be investigated following two different approaches: 1. Constant catalyst weight and different methane flow, 2. Constant methane flow rate and different catalyst weight. Fig. 3. Indicates that regardless of the method adopted to modify the space velocity, increasing this parameter causes a reduction in methane

conversion. By increasing methane flow rate at a constant catalyst weight or decreasing catalyst weight at a constant methane flow rate, a reduction in methane conversion is observed under shorter residence time conditions. In other words, a lower methane decomposition is obtained due to the reduced contact efficiency between the gas and the carbon catalyst. As shown in Fig. 3, at the temperature range of 800–850 °C, methane conversion would remain below 30 vol%, if a space velocity of more than 1 L/g.h is considered for the pure methane. The lines in Fig. 3 (a,b) just show the trends of changing methane conversion during 150 min while in Fig. 3(c-f) the dot-lines represents both the experimental data and the trends.

3.4. Feedstock purity

Although increasing the space velocity through reducing the catalyst weight or increasing the methane flow rate causes a reduction in methane conversion, in some cases due to the some limitations, working

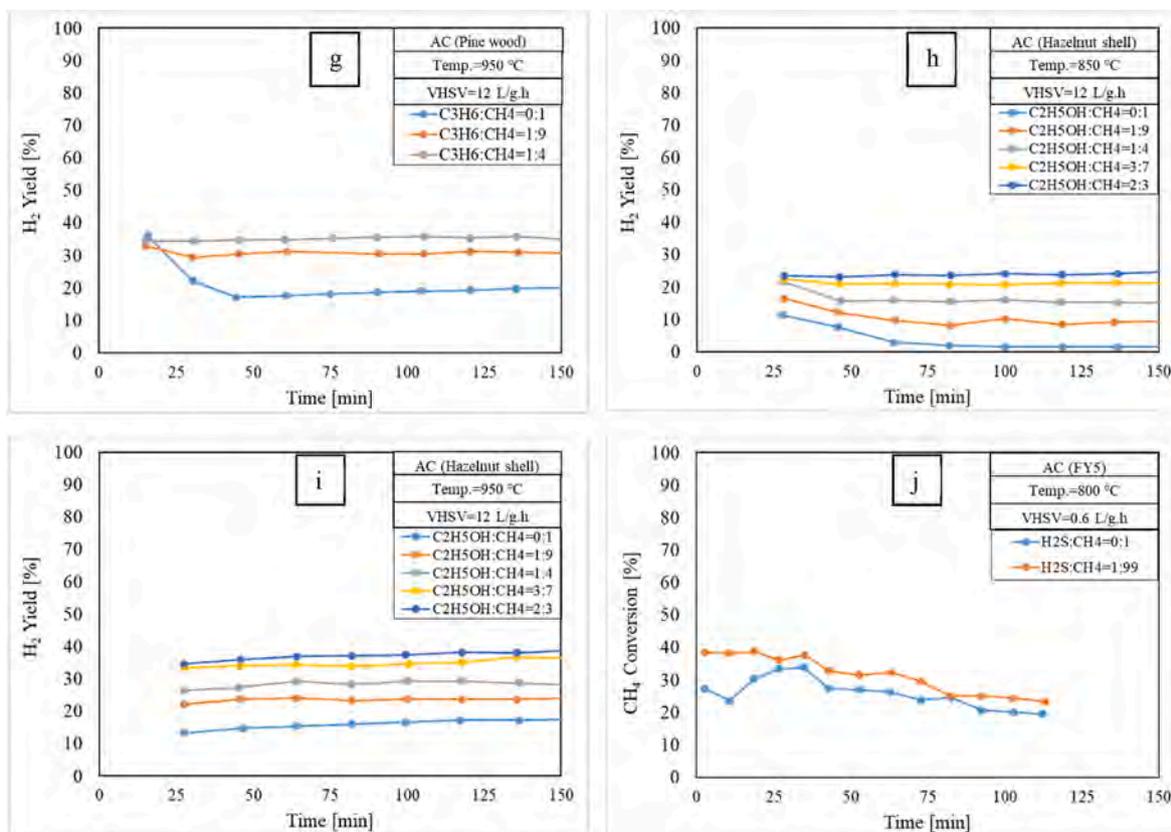


Fig. 5. (continued).

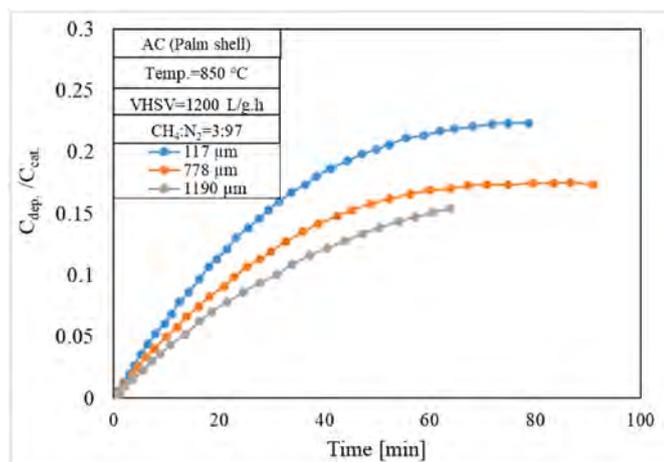


Fig. 6. Impact of catalyst particle size on carbon deposition [83].

at space velocity under 1 L/g.h is not possible. In this situation, instead of pure methane, a gas mixture including methane and an inert carrier gas like nitrogen or helium is used to investigate the methane conversion during the CMD process (see Fig. 4).

Since using natural gas instead of pure methane would be the best option for the industrial production of hydrogen on a commercial scale, some studies have been performed on co-feeding methane with some typical minor components present in natural gas. In these studies, the changes in the yield of hydrogen have been investigated as the result of methane blended with different hydrocarbons such as ethane [77,78], propane [78,79], ethylene [49], propylene [80], and ethanol [77] as well as H₂S [78]. The typical composition of natural gas was reported in Table 4. Based on the results of the literature, which have are

summarized in Fig. 5(a–j), using methane together with heavier hydrocarbons and H₂S can generally have a beneficial effect and promote the hydrogen yield. Thus, it is expected that using natural gas, which is a mixture of methane and a minor amount of other hydrocarbons as well as H₂S and N₂, could be considered for future scale-up processes of CMD: however, it should be observed that purification of hydrogen produced from natural gas due to the presence of additional components could be more difficult. This also depends on the final destination of the produced hydrogen.

4. Effect of catalyst characteristics

Carbon-based catalyst can play a key role in methane cracking. Using a carbon material as catalyst in the CMD process not only helps to obtain hydrogen as an alternative clean and sustainable energy vector but also even the carbon obtained would be a marketable by-product, and represent a permanent sequestration of Carbon. In addition to the operating parameters, the characteristics of the catalyst - such as particle size, surface area, pore volume, oxygenated compounds, and ash content - directly impact the amount of methane conversion. Although some of these features are highly dependent on the nature of the carbon material used as catalyst, they could be improved to some extent by modifying the operating parameters during the activation stage.

4.1. Particle size

Since particle size has an impact on mass transfer and reaction rate, using catalysts with larger particle size leads to a growth in the resistance of internal mass transfer as well as a lower reaction rate and finally in a reduction of methane decomposition. Fig. 6 describes a growth in the weight of carbon deposited over a carbon-based catalyst when the particle size of catalysts reduces from 1190 micro-meter to 117 micro-meter [83]. The results of this study confirm that using catalysts with

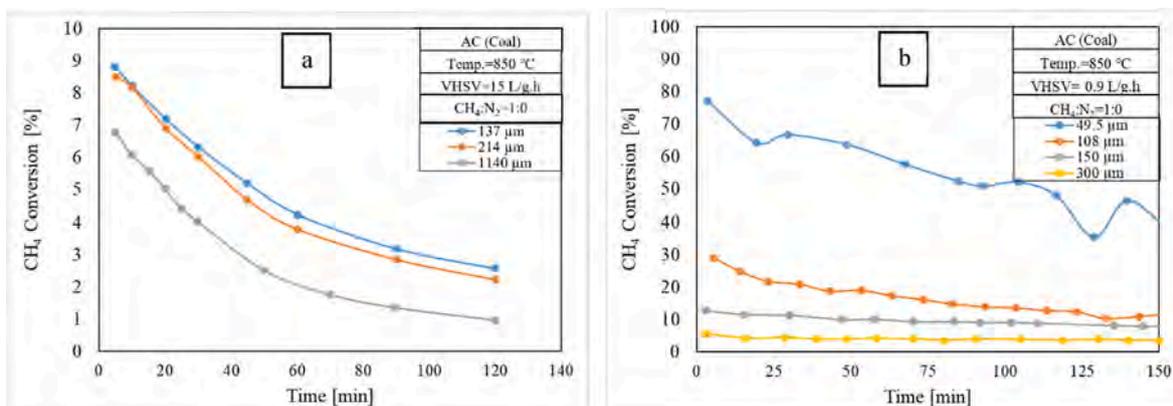


Fig. 7. Impact of catalyst particle size on methane decomposition in presence of carbon-based catalysts, (a): [63], (b): [51].

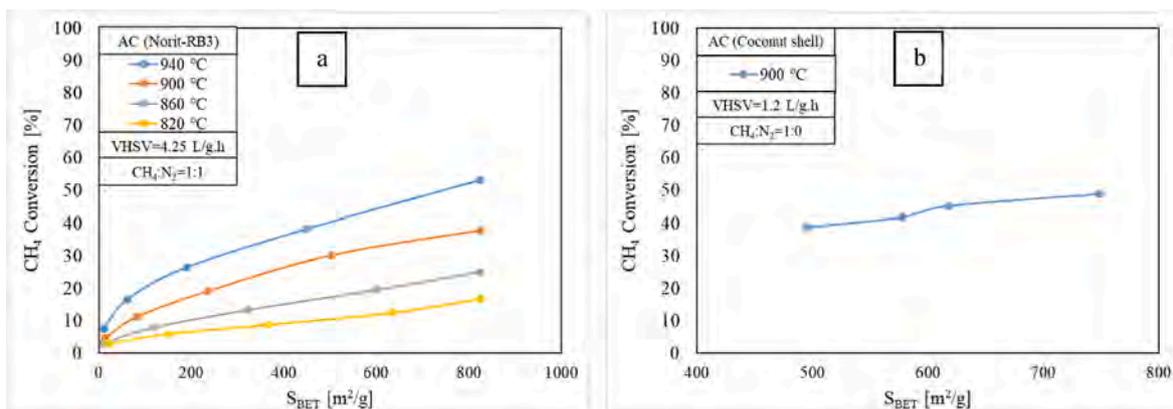


Fig. 8. Impact of carbon-based catalyst surface area on methane decomposition, (a): [69], (b): [87].

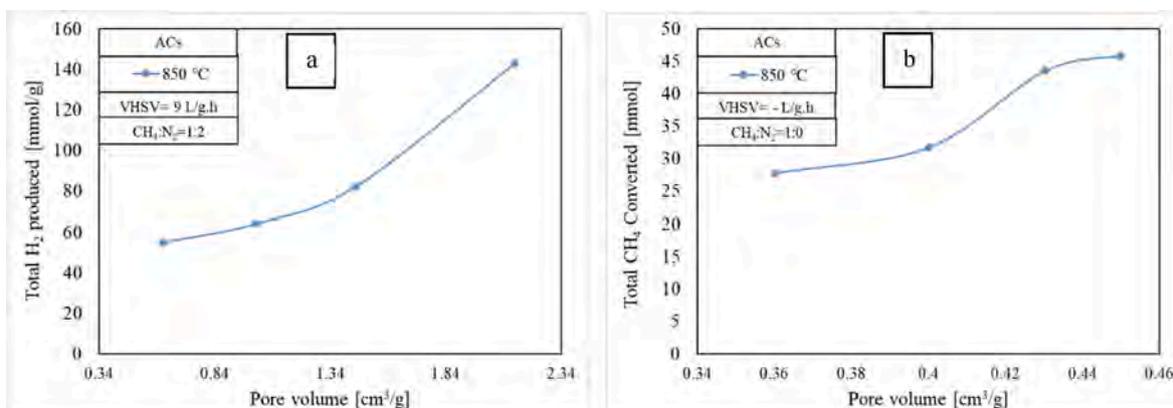


Fig. 9. Impact of carbon-based catalyst pore volume on (a): total H_2 produced [62], (b): total CH_4 converted [86].

lower particle size can offer a larger surface and facilitate mass transfer, and as a result, enhance methane conversion. Also, increasing methane cracking by reducing the catalyst particle size has been reported in some other studies (Fig. 7) [51,63]. Although using carbon-based catalysts with smaller particle sizes can help methane conversion, it should be noted that smaller catalysts provide a higher pressure drop inside the reactor. Figs. 6 and 7 show that particle size in the range of 50–1200 micro-meter has mostly been selected for the CMD process.

4.2. Surface area and pore volume

The impact of surface area on the initial reaction rate has been

investigated in many studies, with contradictive results. On one side, a good correlation between the initial reaction rate and the surface area of the catalyst has been observed which shows a higher rate of methane decomposition could be achieved by using carbon-based catalysts with higher surface area [28,35,49,59,84]. On the other hand, the results of other studies carried out in this area show no discernible trend between surface area and methane reaction rate [30,63,85,86].

Based on the experiments performed on methane cracking over catalysts with different surface areas, Al-Hassani et al. [69] and Liu et al. [87] have claimed that higher methane conversion would be achieved by increasing the surface area of carbon-based catalysts up to $800 \text{ m}^2/\text{g}$ (Fig. 8).

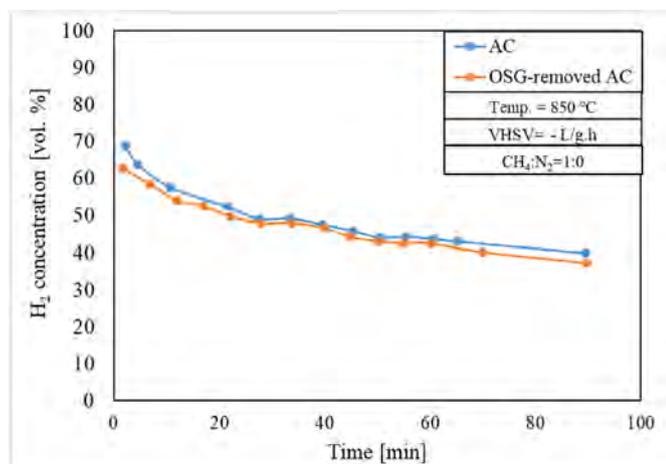


Fig. 10. Impact of OSG of carbon-based catalysts on hydrogen concentration [28].

Also, as shown in Fig. 9, the investigations on the effect of catalyst pore volume on hydrogen yield indicate that increasing the pore volume of the catalyst leads to growth in the total amount of methane converted and total hydrogen produced [62,86].

The studies related to the impact of catalyst pore size on methane conversion show that catalysts with higher meso- and macropores can offer higher methane conversion compared to those having higher micropores [88,89], as micropores provide greater resistance to the diffusion of methane molecules that causes lower hydrogen production [16].

4.3. Oxygenated surface groups (OSG)

In a number of studies, a link between the catalytic properties of carbon materials and the presence of oxygenated surface groups has been observed. Two different mechanisms can explain their influence: (a). Oxygenated groups can directly react with methane molecules, (b). They can be released from the surface as CO and/or CO₂ and create active reaction sites [30]. In some studies, an approximately linear correlation between the initial methane conversion rate and the OSG concentration desorbed as CO and CO₂ has been reported [30,38,85], whereas in another research a positive correlation between the initial reaction rate and only the concentration of CO desorbed has been observed, while oxygenated groups released as CO₂ do not show any effect on the initial reaction rate [31]. According to the study performed by Muradov et al., as in Fig. 10, removing OSG from activated carbon causes a reduction in the concentration of H₂ produced through the CMD process [28].

4.4. Ash content

The impurities in the carbon materials can change the catalytic activity during the CMD process: thus, the impact of different types of impurities and their amount in the carbon-based catalysts on methane conversion has been widely discussed in the literature.

Since most ashes contain a significant amount of heavy metals, and given the fact that metals can efficiently catalyze methane decomposition, it is expected that impurities in the metal forms can lead to an improvement in catalytic activity of carbon materials. Two techniques have been performed to investigate the effect of different metals on carbon catalysts activity in CMD process. First method is removing the metals from the carbon materials with high ash content including different metals through acid treatment and the other one is doping different metals on the low-ash content carbon-based catalysts and analyze their impacts on methane conversion and the catalytic activity.

Liu et al. noted that removing the metals such as Silicon, Iron, Aluminum, Titanium, Calcium, and Sodium as well as sulfur from carbon-based catalysts is possible through acid treatment by HNO₃. A reduction in methane conversion has been reported by increasing the ratio of HNO₃ to carbon material [87]. Also, as given in Fig. 11(a and b), Kim et al. observed that by removing metals from two different types of carbon materials, coconut shell and coal with 1.84% and 10.2% ash content respectively, methane decomposition reduces [63]. Although it seems reduction of metals was the main reason of reduction in methane conversion, it should be noticed that acid treatment, besides removing metals, can cause a reduction in specific surface area and pore structure [63,87]. Furthermore, since acid treatment cannot selectively remove a metal, it is not possible to determine the impact of a specific metal on catalytic activity of carbon materials. Thus, this method is not suggested for predicting the effect of different metals in carbon-based catalysts on methane conversion.

Lots of research also performed on methane cracking over metal-carbon catalysts and in these studies impact of doping metals such as Iron, Nickel, Aluminum, Calcium, Palladium, and Chromium over carbon materials have been investigated. As shown in Fig. 12, loading Fe, Ni, Al, and Ca on carbon-based catalysts can enhance methane conversion in CMD process [61,90–93]. A reduction in surface area was also reported as the consequence of doping metals on the surface of carbon materials.

Also, an improvement in catalytic activity of carbon materials has been reported through doping Pd and Pt up to 20% and 5% respectively, whereas using Cr has shown opposite trend [95] (Fig. 13).

As given in Fig. 14, comparing the effect of loading 20% of different metals including Ni, Cr, Pt, and Pd on the activity of carbon-based catalysts indicates that carbon material with Ni impurity, show higher catalytic activity compared to those doped with Cr or Pt: however,

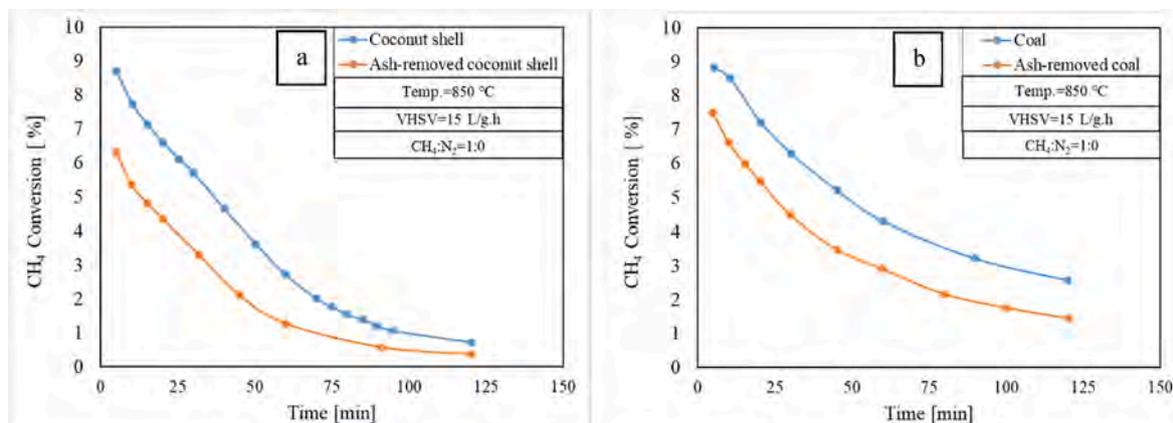


Fig. 11. Impact of carbon-based catalyst impurities on methane conversion, (a) Coconut shell, (b) Coal [63].

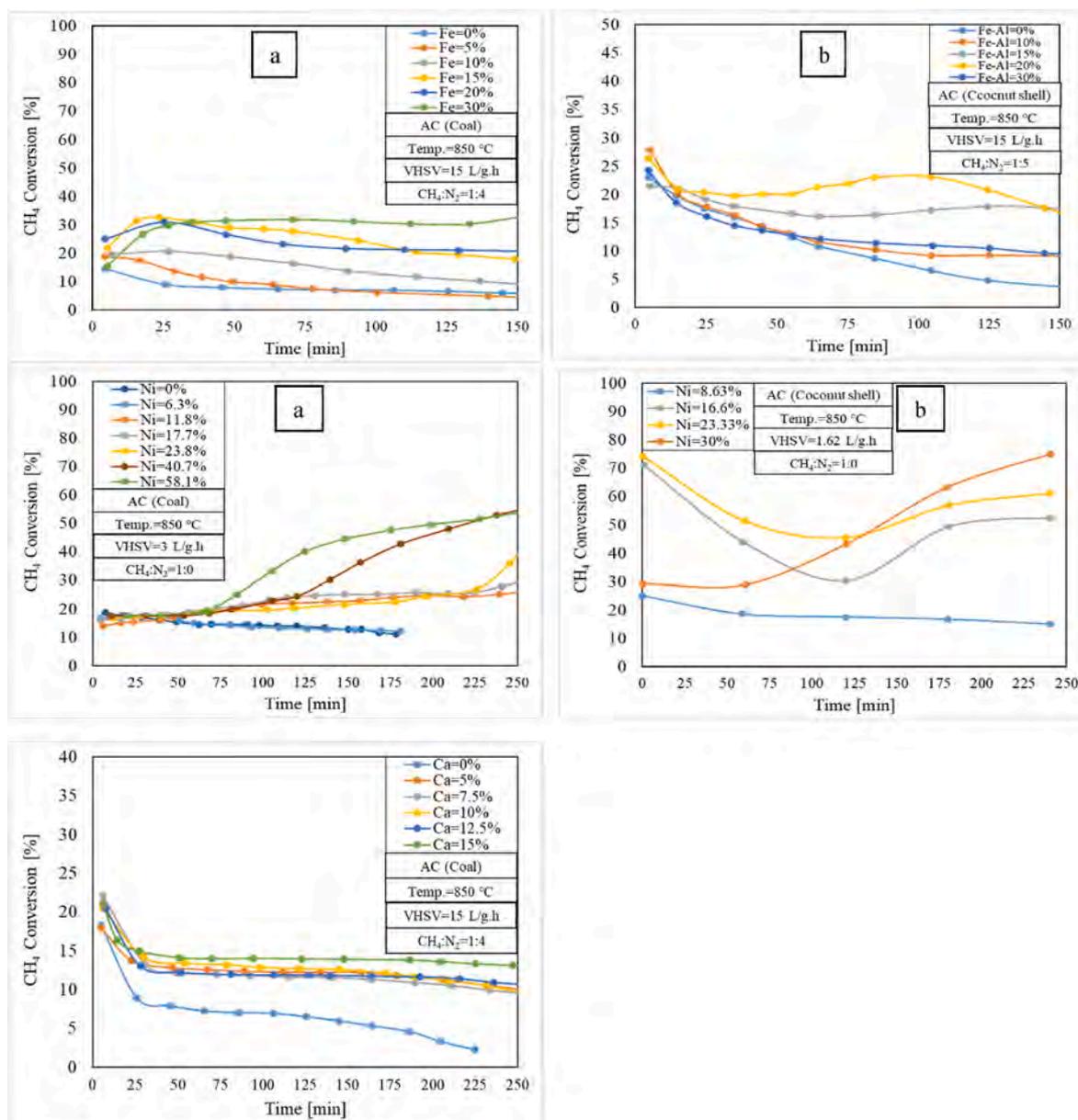


Fig. 12. Impact of doping different metals over carbon-based catalysts on methane conversion over carbon-based catalysts, (a), (b) Fe [61,90], (c), (d) Ni [91,94].

considerably it is lower than the carbon-supported catalyst with Pd impurity.

5. Conclusion

The literature on catalytic decomposition of methane over carbon-based catalysts was extensively reviewed in this paper. The analysis of the main operating parameters such as reaction temperature, pressure, feedstock purity, and space velocity indicated that achieving high methane conversion through the CMD would not be possible unless under optimum operating conditions and over catalysts with suitable characteristics.

As regards the suitable operating temperature for methane cracking, the results of studies show a temperature of more than 800 °C is required for this process. Although an initial methane conversion in the range of 20–30% at 850 °C and 30–40% at 900 °C has generally been reported, initial conversions more than 50% also has been observed at temperature range of 850–900 °C, a fact which could be related to the other operating conditions. Concerning the pressure, since during methane

decomposition the volume of gas is increased, operating at high pressure is not favorable for the CMD process. Also, working under vacuum conditions can be considered just for small-scale reactors, as finding an economic case to work under this condition on a commercial scale is very unlikely. Space velocity is another important operating parameter that could be controlled by changing the total flow rate of feedstock gas or gram of catalyst that is initially loaded. The research work carried out on understanding the effects of this operating parameter show that a space velocity higher than 1 L/g.h, methane conversion cannot be more than 30%. In fact, higher space velocity leads to a reduction in methane conversion due to the corresponding shorter residence time. Given the key relevance of using natural gas for the production of hydrogen on a commercial scale, the impact of minor components present in the natural gas blend on hydrogen yield has been discussed. The results of studies show that the conversion of methane increases during reducing the concentration of methane in feedstock with inert gases. Also, higher hydrogen yield has been observed when methane was mixed with different hydrocarbons such as ethane, propane, ethylene, propylene, and ethanol as well as H₂S. Based on these results, using natural gas – i.e.

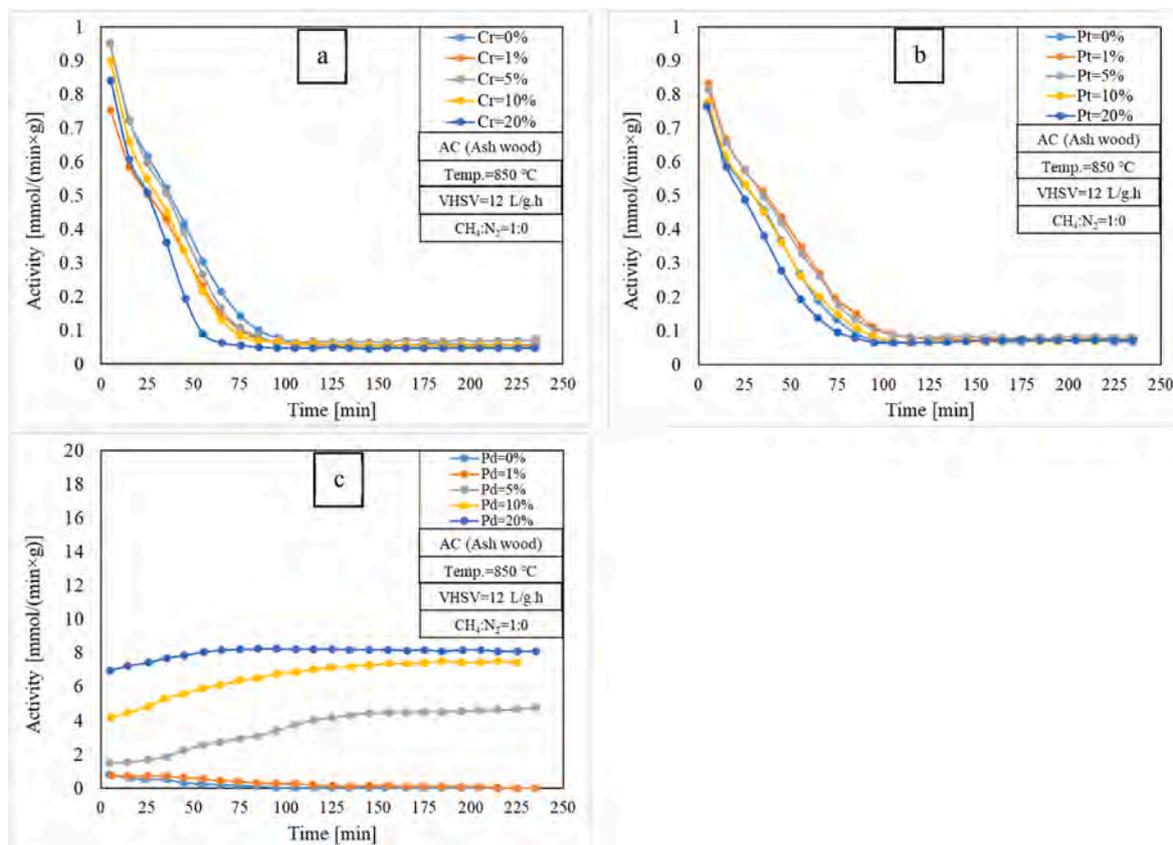


Fig. 13. Impact of doping different metals on the catalytic activity of carbon materials, (a) Cr, (b) Pt, and (c) Pd [95].

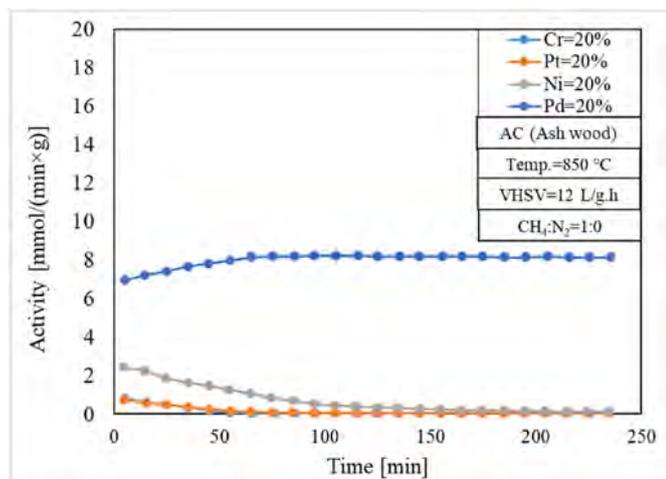


Fig. 14. Comparing the catalytic activity of carbon materials with 20% of Cr, Pt, Ni, and Pd [95].

a mixture of methane and other hydrocarbons as well as H_2S and N_2 - could be considered for future scale-up processes of CMD: however, it should be noticed that probably purification of hydrogen due to the presence of additional components could become more difficult.

In addition to operating parameters, catalyst characteristics such as particle size, surface area, pore volume, oxygenated compounds, and ash content can influence how much methane could be converted. Regarding the particle size of the catalyst, a particle size in the range of 50–1200 micro-meter has been reported for carbon-based catalysts. It should be noticed that although using catalysts with lower particle size can facilitate mass transfer and as a result enhancement in methane

conversion, they can provide higher pressure drop inside the reactor. Concerning the impact of surface area and pore volume on the CMD process, an improvement in hydrogen production and methane conversion has been reported for the carbon materials with higher surface area and pore volume. Furthermore, it has been observed that carbon-based catalysts with higher meso- and macropores can provide higher methane conversion, compared to the high micropores carbon materials. Analysis of the link between oxygenated surface groups and the catalytic activity of the carbon-based catalyst reveals that removing these groups from the surface of carbon materials leads to a reduction in methane conversion. Based on the studies, the impurities especially the metals such as Fe, Ni, Ca, Pt, Pd, and Cr can change the catalytic activity of carbon materials. Since these metals can efficiently catalyze methane decomposition, methane conversion over metal-carbon catalysts produced from loading metals over carbon materials has been investigated in many studies. The result of the analysis show that doping Fe, Ni, Ca, and Pd metals over carbonaceous materials improve their catalytic activities, whereas the opposite trend has been observed when loading Cr. An upward trend has been reported by doping Pt up to 5% over the carbon-based catalysts: however, loading more than 5% has the opposite impact.

In summary, the major findings, which are mostly related to engineering design, are reported as follows.

1. Operating temperature more than $800\text{ }^\circ\text{C}$ and space velocity less than 1 L/g.h for pure methane are required to provide methane conversion higher than 50%.
2. Higher hydrogen yield has been observed when methane was mixed with different hydrocarbons such as ethane, propane, ethylene, propylene, and ethanol as well as H_2S .

- Carbon materials with lower particle size, higher surface area and mesopores, and more oxygenated compounds show higher catalytic activity in CMD process.
- Doping metals such as Fe, Ni, Ca, and Pd over carbon-based catalysts can lead to an improvement in methane conversion while loading Cr on carbon materials has adverse impacts on catalytic activity of these materials. An upward trend has been reported by doping Pt up to 5% over the carbon-based catalysts: however, loading more than 5% has the opposite impact.

Although lots of studies have been performed on the pyrolysis of methane at different operating conditions over various carbon-based catalysts, there is still a research gap due to the insufficient data in the following subjects.

- Effect of inlet gas temperature on methane conversion
- A comprehensive techno-economic analysis of hydrogen production through thermo-chemical decomposition of natural gas over carbon-based catalysts
- Investigation on operating conditions of carbon materials (biochar) production process and its impact on characteristics carbon-based catalysts
- Impact of different activation methods on catalytic activity of carbon materials

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: David Chiamonti (H2STEEL proj coordinator) reports financial support was provided by European Innovation Council.

Data availability

No data was used for the research described in the article.

Acknowledgements

This work was supported by the European Innovation Council (EIC) through the “H2STEEL project”, Grant number 101070741.

References

- Chen L, Qi Z, Zhang S, Su J, Somorjai GA. Catalytic hydrogen production from methane. 2020.
- Marbán G, Valdés-Solis T. Towards the hydrogen economy? Int J Hydrogen Energy 2007;32(12):1625–37. <https://doi.org/10.1016/j.ijhydene.2006.12.017>.
- Iulianelli A, Liguori S, Wilcox J, Basile A. Advances on methane steam reforming to produce hydrogen through membrane reactors technology: a review. Catal Rev - Sci Eng 2016;58(1):1–35. <https://doi.org/10.1080/01614940.2015.1099882>.
- Srilatha K, Bhagawan D, Shiva Kumar S, Himabindu V. Sustainable fuel production by thermocatalytic decomposition of methane – a review. South Afr J Chem Eng 2017;24(October):156–67. <https://doi.org/10.1016/j.sajce.2017.10.002>.
- Usman M, Wan Daud WMA, Abbas HF. Dry reforming of methane: influence of process parameters - a review. Renew Sustain Energy Rev 2015;45:710–44. <https://doi.org/10.1016/j.rser.2015.02.026>.
- Sánchez-Bastardo N, Schlögl R, Ruland H. Methane pyrolysis for zero-emission hydrogen production: a potential bridge technology from fossil fuels to a renewable and sustainable hydrogen economy. Ind Eng Chem Res 2021;60(32):11855–81. <https://doi.org/10.1021/acs.iecr.1c01679>.
- Parkinson B, et al. Hydrogen production using methane: techno-economics of decarbonizing fuels and chemicals. Int J Hydrogen Energy 2018;43(5):2540–55. <https://doi.org/10.1016/j.ijhydene.2017.12.081>.
- Oni AO, Anaya K, Giwa T, Di Lullo G, Kumar A. Comparative assessment of blue hydrogen from steam methane reforming, autothermal reforming, and natural gas decomposition technologies for natural gas-producing regions. Energy Convers Manag 2022;254:115245. <https://doi.org/10.1016/j.enconman.2022.115245>.
- Terlouw T, Bauer C. Environmental Science electrolysis: a techno-economic and environmental assessment †. 2022. p. 3583–602. <https://doi.org/10.1039/d2ee01023b>.
- Motazedi K, Khojasteh Y, Laurenzi LJ, Maclean HL, Bergerson JA. ScienceDirect Economic and environmental competitiveness of high temperature electrolysis for hydrogen production. Int J Hydrogen Energy 2021;46(41):21274–88. <https://doi.org/10.1016/j.ijhydene.2021.03.226>.
- Machhammer O, Bode A, Hormuth W. Financial and ecological evaluation of hydrogen production processes on large scale. Chem Eng Technol 2016;39(6):1185–93. <https://doi.org/10.1002/ceat.201600023>.
- Musamali R, Isa YM. Decomposition of methane to carbon and hydrogen: a catalytic perspective. Energy Technol 2019;7(6):1–16. <https://doi.org/10.1002/ente.201800593>.
- Msheik M, Rodat S, Abanades S. Methane cracking for hydrogen production: a review of catalytic and molten media pyrolysis. Energies 2021;14(11). <https://doi.org/10.3390/en14113107>.
- Riley J, Atallah C, Siriwardane R, Stevens R. ScienceDirect Technoeconomic analysis for hydrogen and carbon Co-Production via catalytic pyrolysis of methane. Int J Hydrogen Energy 2021;46(39):20338–58. <https://doi.org/10.1016/j.ijhydene.2021.03.151>.
- Keipi T, Tolvanen KES, Tolvanen H, Konttinen J. Thermo-catalytic decomposition of methane: the effect of reaction parameters on process design and the utilization possibilities of the produced carbon. Energy Convers Manag 2016;126:923–34. <https://doi.org/10.1016/j.enconman.2016.08.060>.
- Zhang J, et al. Hydrogen production by catalytic methane decomposition: carbon materials as catalysts or catalyst supports. Int J Hydrogen Energy 2017;42(31):19755–75. <https://doi.org/10.1016/j.ijhydene.2017.06.197>.
- Chaubey R, Sahu S, James OO, Maity S. A review on development of industrial processes and emerging techniques for production of hydrogen from renewable and sustainable sources. Renew Sustain Energy Rev 2013;23:443–62. <https://doi.org/10.1016/j.rser.2013.02.019>.
- Ashik UPM, Wan Daud WMA, Abbas HF. Production of greenhouse gas free hydrogen by thermocatalytic decomposition of methane - a review. Renew Sustain Energy Rev 2015;44:221–56. <https://doi.org/10.1016/j.rser.2014.12.025>.
- Schneider S, Bajohr S, Graf F, Kolb T. State of the art of hydrogen production via pyrolysis of natural gas. ChemBioEng Rev 2020;7(5):150–8. <https://doi.org/10.1002/cben.202000014>.
- Pudukudy M, Yaakob Z, Jia Q, Sobri Takriff M. Catalytic decomposition of undiluted methane into hydrogen and carbon nanotubes over Pt promoted Ni/CeO2 catalysts. New J Chem 2018;42(18):14843–56. <https://doi.org/10.1039/c8nj02842g>.
- Dagle R, Dagle V, Bearden M, Holladay J, Krause T, Ahmed S. R&D Opportunities for Development of Natural Gas Conversion Technologies for Co-Production of Hydrogen and value-added solid carbon products. Argonne Natl Lab Rep 2017: 1–73.
- Muller-Syring G, Große C, Eysser M, Glandien J, Schütz S. Critical evaluation of default values for the GHG emissions of the natural gas supply chain. Int. Gas Res. Conf. Proc. 2017;1:131–5.
- Timmerberg S, Kaltschmitt M, Finkbeiner M. Hydrogen and hydrogen-derived fuels through methane decomposition of natural gas – GHG emissions and costs. Energy Convers Manag X 2020;7(April):100043. <https://doi.org/10.1016/j.ecmx.2020.100043>.
- Sánchez-Bastardo N, Schlögl R, Ruland H. Methane pyrolysis for CO2-free H2 production: a green process to overcome renewable energies unsteadiness. Chem-Ing-Tech 2020;92(10):1596–609. <https://doi.org/10.1002/cite.202000029>.
- Riley J, Atallah C, Siriwardane R, Stevens R. Technoeconomic analysis for hydrogen and carbon Co-Production via catalytic pyrolysis of methane. Int J Hydrogen Energy 2021;46(39):20338–58. <https://doi.org/10.1016/j.ijhydene.2021.03.151>.
- Li Y, Yu H, Jiang X, Deng G, Wen JZ, Tan Z. Techno-economic analysis for hydrogen-burning power plant with onsite hydrogen production unit based on methane catalytic decomposition. Energy Convers Manag 2023;277(January): 116674. <https://doi.org/10.1016/j.enconman.2023.116674>.
- Abbas HF, Wan Daud WMA. Hydrogen production by methane decomposition: a review. Int J Hydrogen Energy 2010;35(3):1160–90. <https://doi.org/10.1016/j.ijhydene.2009.11.036>.
- Muradov N, Smith F, T-Raissi A. Catalytic activity of carbons for methane decomposition reaction. Catal Today 2005;102(103):225–33. <https://doi.org/10.1016/j.cattod.2005.02.018>.
- Dufour A, Celzard A, Fierro V, Martin E, Broust F, Zoulalian A. Catalytic decomposition of methane over a wood char concurrently activated by a pyrolysis gas. Appl Catal Gen 2008;346(1–2):164–73. <https://doi.org/10.1016/j.apcata.2008.05.023>.
- Moliner R, Suelves I, Lázaro MJ, Moreno O. Thermocatalytic decomposition of methane over activated carbons: influence of textural properties and surface chemistry. Int J Hydrogen Energy 2005;30(3):293–300. <https://doi.org/10.1016/j.ijhydene.2004.03.035>.
- Suelves I, Pinilla JL, Lázaro MJ, Moliner R. Carbonaceous materials as catalysts for decomposition of methane. Chem Eng J 2008;140(1–3):432–8. <https://doi.org/10.1016/j.cej.2007.11.014>.
- Lee EK, et al. Catalytic decomposition of methane over carbon blacks for CO 2-free hydrogen production. Carbon N. Y. 2004;42(12–13):2641–8. <https://doi.org/10.1016/j.carbon.2004.06.003>.
- Serrano DP, Botas JA, Pizarro P, Guil-López R, Gómez G. Ordered mesoporous carbons as highly active catalysts for hydrogen production by CH4 decomposition. Chem Commun 2008;48:6585–7. <https://doi.org/10.1039/b811800k>.
- Serrano DP, Botas JA, Guil-Lopez R. H2 production from methane pyrolysis over commercial carbon catalysts: kinetic and deactivation study. Int J Hydrogen Energy 2009;34(10):4488–94. <https://doi.org/10.1016/j.ijhydene.2008.07.079>.
- Muradov N. Catalysis of methane decomposition over elemental carbon. Catal Commun 2001;2(3–4):89–94. [https://doi.org/10.1016/S1566-7367\(01\)00013-9](https://doi.org/10.1016/S1566-7367(01)00013-9).

- [36] Guil-Lopez R, Botas JA, Fierro JLG, Serrano DP. Comparison of metal and carbon catalysts for hydrogen production by methane decomposition. *Appl Catal Gen* 2011;396(1–2):40–51. <https://doi.org/10.1016/j.apcata.2011.01.036>.
- [37] Albrecht M, Rodemerck U, Linke D, Kondratenko EV. Oxidative coupling of methane at elevated pressures: reactor concept and its validation. *React Chem Eng* 2018;3(2):151–4. <https://doi.org/10.1039/c7re00208d>.
- [38] Pinilla JL, Suelves I, Utrilla R, Gálvez ME, Lázaro MJ, Moliner R. Hydrogen production by thermo-catalytic decomposition of methane: regeneration of active carbons using CO₂. *J Power Sources* 2007;169(1):103–9. <https://doi.org/10.1016/j.jpowsour.2007.01.045>.
- [39] Qiu XQ, Zhu QM, Wong NB, Tin KC. Catalytic contribution of reactor wall materials on oxidative coupling of methane. *J Chem Technol Biotechnol* 1996;65(4):380–4. [https://doi.org/10.1002/\(sici\)1097-4660\(199604\)65:4<380::aid-jctb452>3.0.co;2-7](https://doi.org/10.1002/(sici)1097-4660(199604)65:4<380::aid-jctb452>3.0.co;2-7).
- [40] Sadjadi S, Simon U, Godini HR, Görke O, Schomäcker R, Wozny G. Reactor material and gas dilution effects on the performance of miniplant-scale fluidized-bed reactors for oxidative coupling of methane. *Chem Eng J* 2015;281:678–87. <https://doi.org/10.1016/j.cej.2015.06.079>.
- [41] Pham CQ, et al. Production of hydrogen and value-added carbon materials by catalytic methane decomposition: a review. *Environ Chem Lett* 2022;20(4):2339–59. <https://doi.org/10.1007/s10311-022-01449-2>.
- [42] Raza J, et al. Methane decomposition for hydrogen production: a comprehensive review on catalyst selection and reactor systems. *Renew Sustain Energy Rev* 2022;168(June):112774. <https://doi.org/10.1016/j.rser.2022.112774>.
- [43] Pudukudy M, Kadier A, Yaakob Z, Takriff MS. Non-oxidative thermocatalytic decomposition of methane into CO_x free hydrogen and nanocarbon over unsupported porous NiO and Fe₂O₃ catalysts. *Int J Hydrogen Energy* 2016;41(41):18509–21. <https://doi.org/10.1016/j.ijhydene.2016.08.160>.
- [44] Raza J, et al. Methane decomposition for hydrogen production over biomass fly ash-based CeO₂ nanowires promoted cobalt catalyst. *J Environ Chem Eng* 2021;9(5):105816. <https://doi.org/10.1016/j.jece.2021.105816>.
- [45] Awadallah AE, Aboul-Enein AA, Mahmoud AH, Abd El Rehim SS, El-Ziati AK, Aboul-Gheit AK. ZrxMg1-xO supported cobalt catalysts for methane decomposition into CO_x-free hydrogen and carbon nanotubes. *Int J Green Energy* 2018;15(10):568–76. <https://doi.org/10.1080/15435075.2018.1510407>.
- [46] Awadallah AE, El-Desouki DS, Abdel-Aziz SM, Aboul-Gheit NAK, Abdel-Hamid SM, Aboul-Gheit AK. Effect of La, Ce and Nd oxides addition on the activity and stability of Co/MgO catalyst for methane decomposition into CO_x-free H₂ production and carbon nanotubes. *Fullerenes, Nanotub Carbon Nanostruct* 2018;26(9):525–34. <https://doi.org/10.1080/1536383X.2018.1455666>.
- [47] Dunker AM, Kumar S, Mulawa PA. Production of hydrogen by thermal decomposition of methane in a fluidized-bed reactor - effects of catalyst, temperature, and residence time. *Int J Hydrogen Energy* 2006;31(4):473–84. <https://doi.org/10.1016/j.ijhydene.2005.04.023>.
- [48] Rashidi A, Lotfi R, Fakhrosavi E, Zare M. Production of single-walled carbon nanotubes from methane over Co-Mo/MgO nanocatalyst: a comparative study of fixed and fluidized bed reactors. *J Nat Gas Chem* 2011;20(4):372–6. [https://doi.org/10.1016/S1003-9953\(10\)60208-3](https://doi.org/10.1016/S1003-9953(10)60208-3).
- [49] Muradov N. Hydrogen via methane decomposition: an application for decarbonization of fossil fuels. *Int J Hydrogen Energy* 2001;26(11):1165–75. [https://doi.org/10.1016/S0360-3199\(01\)00073-8](https://doi.org/10.1016/S0360-3199(01)00073-8).
- [50] Muradov N, Chen Z, Smith F. Fossil hydrogen with reduced CO₂ emission: modeling thermocatalytic decomposition of methane in a fluidized bed of carbon particles. *Int J Hydrogen Energy* 2005;30(10):1149–58. <https://doi.org/10.1016/j.ijhydene.2005.04.005>.
- [51] Kyu K, Young G, June K, Kwon B. Thermocatalytic hydrogen production from the methane in a fluidized bed with activated carbon catalyst, vol. 95; 2004. p. 81–6. <https://doi.org/10.1016/j.cattod.2004.06.080>.
- [52] Cadoret L, et al. Silicon Chemical Vapor Deposition on macro and submicron powders in a fluidized bed. *Powder Technol* 2009;190(1–2):185–91. <https://doi.org/10.1016/j.powtec.2008.04.083>.
- [53] Geißler T, et al. Hydrogen production via methane pyrolysis in a liquid metal bubble column reactor with a packed bed. *Chem Eng J* 2016;299:192–200. <https://doi.org/10.1016/j.cej.2016.04.066>.
- [54] Wang Y, Yao L, Wang S, Mao D, Hu C. Low-temperature catalytic CO₂ dry reforming of methane on Ni-based catalysts: a review. *Fuel Process Technol* 2018;169(June 2017):199–206. <https://doi.org/10.1016/j.fuproc.2017.10.007>.
- [55] Slovetskii DI. Plasma-chemical processes in petroleum chemistry (review). *Petrol Chem* 2006;46(5):295–304. <https://doi.org/10.1134/S096554410605001X>.
- [56] Nishida Y, Cheng C, Iwasaki K. Use of Plasma Discharges Under High 2014;42(12):1–7.
- [57] Mishra LN, Shibata K, Ito H, Yugami N, Nishida Y. Conversion of methane to hydrogen via pulsed corona discharge. *J Nat Gas Chem* 2004;13(2):82–6.
- [58] Alves L, Pereira V, Lagarteira T. Catalytic methane decomposition to boost the energy transition : scie. ntific and technological advancements Nomenclature 2021;137(September 2020). <https://doi.org/10.1016/j.rser.2020.110465>.
- [59] Ryu BH, Lee SY, Lee DH, Han GY, Lee TJ, Yoon KJ. Catalytic characteristics of various rubber-reinforcing carbon blacks in decomposition of methane for hydrogen production. *Catal Today* 2007;123(1–4):303–9. <https://doi.org/10.1016/j.cattod.2007.02.001>.
- [60] Lee SC, Seo HJ, Han GY. Hydrogen production by catalytic decomposition of methane over carbon black catalyst at high temperatures. *Kor J Chem Eng* 2013;30(9):1716–21. <https://doi.org/10.1007/s11814-013-0107-7>.
- [61] Bai Z, Chen H, Li W, Li B. Hydrogen production by methane decomposition over coal char. *Int J Hydrogen Energy* 2006;31(7):899–905. <https://doi.org/10.1016/j.ijhydene.2005.08.001>.
- [62] Wang HY, Lua AC. Hydrogen production by thermocatalytic methane decomposition. *Heat Tran Eng* 2013;34(11–12):896–903. <https://doi.org/10.1080/01457632.2012.752682>.
- [63] Kim MH, et al. Hydrogen production by catalytic decomposition of methane over activated carbons: kinetic study. *Int J Hydrogen Energy* 2004;29(2):187–93. [https://doi.org/10.1016/S0360-3199\(03\)00111-3](https://doi.org/10.1016/S0360-3199(03)00111-3).
- [64] Bai Z, Chen H, Li B, Li W. Catalytic decomposition of methane over activated carbon. *J Anal Appl Pyrolysis* 2005;73(2):335–41. <https://doi.org/10.1016/j.jaap.2005.03.004>.
- [65] Wei L, Tan YS, Han YZ, Zhao JT, Wu J, Zhang D. Hydrogen production by methane cracking over different coal chars. *Fuel* 2011;90(11):3473–9. <https://doi.org/10.1016/j.fuel.2011.06.053>.
- [66] Bai Z, Chen H, Li B, Li W. Methane decomposition over Ni loaded activated carbon for hydrogen production and the formation of filamentous carbon. *Int J Hydrogen Energy* 2007;32(1):32–7. <https://doi.org/10.1016/j.ijhydene.2006.06.030>.
- [67] Ashok J, Kumar SN, Venugopal A, Kumari VD, Tripathi S, Subrahmanyam M. CO_x free hydrogen by methane decomposition over activated carbons. *Catal Commun* 2008;9(1):164–9. <https://doi.org/10.1016/j.catcom.2007.05.046>.
- [68] Yang L, Liu F, Zhang X, He J, Saito K. Joint-use of activated carbon and carbon black to enhance catalytic stability during chemical looping methane decomposition process. *Int J Hydrogen Energy* 2020;45(24):13245–55. <https://doi.org/10.1016/j.ijhydene.2020.03.055>.
- [69] Al-Hassani AA, Abbas HF, Wan Daud WMA. Production of CO_x-free hydrogen by the thermal decomposition of methane over activated carbon: catalyst deactivation. *Int J Hydrogen Energy* 2014;39(27):14783–91. <https://doi.org/10.1016/j.ijhydene.2014.07.031>.
- [70] Jung JU, Nam W, Yoon KJ, Han GY. Hydrogen production by catalytic decomposition of methane over carbon catalysts in a fluidized bed 2007;24(4):674–8.
- [71] Patel S, et al. Production of hydrogen by catalytic methane decomposition using biochar and activated char produced from biosolids pyrolysis. *Int J Hydrogen Energy* 2020;45(55):29978–92. <https://doi.org/10.1016/j.ijhydene.2020.08.036>.
- [72] Rechia P, Malaika A, Najder-Kozdrowska L, Kozłowski M. The effect of ethanol on carbon-catalysed decomposition of methane. *Int J Hydrogen Energy* 2012;37(9):7512–20. <https://doi.org/10.1016/j.ijhydene.2012.02.014>.
- [73] Younesi-Sinaki M, Matida EA, Hamdullahpur F. Kinetic model of homogeneous thermal decomposition of methane and ethane. *Int J Hydrogen Energy* 2009;34(9):3710–6. <https://doi.org/10.1016/j.ijhydene.2009.03.014>.
- [74] Chen Z, et al. Vacuum promoted methane decomposition for hydrogen production with carbon separation: parameter optimization and economic assessment. *Energy* 2021;222. <https://doi.org/10.1016/j.energy.2021.119953>.
- [75] Abbas HF, Daud WMAW. Influence of reactor material and activated carbon on the thermocatalytic decomposition of methane for hydrogen production. *Appl Catal Gen* 2010;388(1–2):232–9. <https://doi.org/10.1016/j.apcata.2010.08.057>.
- [76] Domínguez A, Fidalgo B, Fernández Y, Pis JJ, Menéndez JA. Microwave-assisted catalytic decomposition of methane over activated carbon for CO₂-free hydrogen production. *Int J Hydrogen Energy* 2007;32(18):4792–9. <https://doi.org/10.1016/j.ijhydene.2007.07.041>.
- [77] Rechia P, Malaika A, Krzyżyńska B, Kozłowski M. Decomposition of methane in the presence of ethanol over activated carbon catalyst. *Int J Hydrogen Energy* 2012;37(19):14178–86. <https://doi.org/10.1016/j.ijhydene.2012.07.060>.
- [78] Fidalgo B, Muradov N, Menéndez JA. Effect of H₂S on carbon-catalysed methane decomposition and CO₂ reforming reactions. *Int J Hydrogen Energy* 2012;37(19):14187–94. <https://doi.org/10.1016/j.ijhydene.2012.07.090>.
- [79] Pinilla JL, Suelves I, Lázaro MJ, Moliner R. Influence on hydrogen production of the minor components of natural gas during its decomposition using carbonaceous catalysts. *J Power Sources* 2009;192(1):100–6. <https://doi.org/10.1016/j.jpowsour.2008.12.074>.
- [80] Malaika A, Kozłowski M. Influence of ethylene on carbon-catalysed decomposition of methane. *Int J Hydrogen Energy* 2009;34(6):2600–5. <https://doi.org/10.1016/j.ijhydene.2009.01.052>.
- [81] Christina Ingo MB-S, Tuuf Jessica. Impact of hydrogen on natural gas compositions to meet engine gas quality requirements. 2022.
- [82] Malaika A, Kozłowski M. Hydrogen production by propylene-assisted decomposition of methane over activated carbon catalysts. *Int J Hydrogen Energy* 2010;35(19):10302–10. <https://doi.org/10.1016/j.ijhydene.2010.07.176>.
- [83] Abbas HF, Wan Daud WMA. Thermocatalytic decomposition of methane using palm shell based activated carbon: kinetic and deactivation studies. *Fuel Process Technol* 2009;90(9):1167–74. <https://doi.org/10.1016/j.fuproc.2009.05.024>.
- [84] Lee SY, Ryu BH, Han GY, Lee TJ, Yoon KJ. Catalytic characteristics of specialty carbon blacks in decomposition of methane for hydrogen production. *Carbon N. Y.* 2008;46(14):1978–86. <https://doi.org/10.1016/j.carbon.2008.08.008>.
- [85] Suelves I, Lázaro MJ, Moliner R, Pinilla JL, Cubero H. Hydrogen production by methane decarbonization: carbonaceous catalysts. *Int J Hydrogen Energy* 2007;32(15 SPEC. ISS):3320–6. <https://doi.org/10.1016/j.ijhydene.2007.05.028>.
- [86] Bai Z, Li W, Bai J, Li B, Chen H. The effects of textural properties and surface chemistry of activated carbon on its catalytic performance in methane decomposition for hydrogen production. *Energy Sources, Part A Recover Util Environ Eff* 2012;34(12):1145–53. <https://doi.org/10.1080/15567031003663174>.
- [87] Liu F, Xuan G, Ai L, Liu Q, Yang L. Key factors that affect catalytic activity of activated carbon-based catalyst in chemical looping methane decomposition for H₂ production. *Fuel Process Technol* 2021;215(January). <https://doi.org/10.1016/j.fuproc.2021.106745>.
- [88] Srilatha K, Viditha V, Srinivasulu D, Ramakrishna SUB, Himabindu V. Hydrogen production using thermocatalytic decomposition of methane on Ni30/activated

- carbon and Ni₃₀/carbon black. *Environ Sci Pollut Res* 2016;23(10):9303–11. <https://doi.org/10.1007/s11356-015-5112-4>.
- [89] Wang Y, et al. Effect of mineral in coal on preparation of activated carbon for methane decomposition to hydrogen. *Fuel* 2019;258(April):116138. <https://doi.org/10.1016/j.fuel.2019.116138>.
- [90] Wang J, Jin L, Li Y, Hu H. Preparation of Fe-doped carbon catalyst for methane decomposition to hydrogen. *Ind Eng Chem Res* 2017;56(39):11021–7. <https://doi.org/10.1021/acs.iecr.7b02394>.
- [91] Zhang J, Jin L, Li Y, Hu H. Ni doped carbons for hydrogen production by catalytic methane decomposition. *Int J Hydrogen Energy* 2013;38(10):3937–47. <https://doi.org/10.1016/j.ijhydene.2013.01.105>.
- [92] Zhang J, Jin L, Li Y, Si H, Qiu B, Hu H. Hierarchical porous carbon catalyst for simultaneous preparation of hydrogen and fibrous carbon by catalytic methane decomposition. *Int J Hydrogen Energy* 2013;38(21):8732–40. <https://doi.org/10.1016/j.ijhydene.2013.05.012>.
- [93] Wang J, Jin L, Zhou Y, Li Y, Hu H. Effect of Ca(NO₃)₂ addition in coal on properties of activated carbon for methane decomposition to hydrogen. *Fuel Process Technol* 2018;176(January):85–90. <https://doi.org/10.1016/j.fuproc.2018.03.012>.
- [94] Sarada Prasad J, Dhand V, Himabindu V, Anjaneyulu Y. Production of hydrogen and carbon nanofibers through the decomposition of methane over activated carbon supported Ni catalysts. *Int J Hydrogen Energy* 2011;36(18):11702–11. <https://doi.org/10.1016/j.ijhydene.2011.05.176>.
- [95] Szymańska M, Malaika A, Rechnia P, Miklaszewska A, Kozłowski M. Metal/activated carbon systems as catalysts of methane decomposition reaction. *Catal Today* 2015;249:94–102. <https://doi.org/10.1016/j.cattod.2014.11.025>.