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Chapter

Sustainability Effect of Water Gas Shift Reaction (Syngas) in Catalytic Upgrading of Heavy Crude Oil and Bitumen

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Abstract

Industrial globalization and urbanization has placed man on a path for the quest of energy. Conspicuously there are various types and forms of energy with established technologies on harnessing and utilization wherein fossil fuel still remains the cheapest with straightforward application. Although, conventional fossil fuel resources are depleting because of population growth, unconventional reservoirs are exploited daily with limited production due to inadequate and expensive technology making them stand at approximately 9.1 trillion barrels poised to quell the world's energy insecurity for the next 100 years. The underlying basis for the high-cost of unconventional reservoirs upgrading is the hydrogen required to seal the alkyl chain after cracking to form low molecular weight hydrocarbons. Therefore, in this chapter we aim to provide a comprehensive review of in-situ generation of hydrogen from syngas via water gas shift reaction for the catalytic upgrading of heavy crude oil and bitumen by analyzing the gas chromatography results of gaseous effluents for the presence of syngas in the various works cited. Although, heavy crude oil and bitumen are non-renewable the upgrading method selected is tenable, appropriately the overall technology is partially sustainable.

Keywords: fuel, syngas, water gas shift reaction, heavy crude oil, bitumen, hydrogen, gas chromatography, sustainability

1. Introduction

Synthesis gas (Syngas) is a gas mixture containing carbon monoxide (CO) and hydrogen (H₂) in dissimilar proportions produced from gasification of a carbon-containing material to gaseous products [1]. Also, water gas reaction (WGR) is a mixture of carbon monoxide and hydrogen produced by passing steam over red-hot coke in an endothermic reaction (Eq. 1).



Reaction 3 in the above mechanism is foremost in order to shift the carbon monoxide entirely to hydrogen in the presence of an oxide based catalyst. This reaction can be applied separately and it is called the water gas shift reaction (WGSR) [2]. Detailed reaction mechanism for syngas production is displayed in **Table 1** to depict where all these fit in.

Reactions in syngas production follows series of steps subdivided into; reforming, oxidation and carbon forming with water gas shift passing off as a very rapid equilibrium reaction step. These three distinct reactions are independent in their own right and characterized by the reaction condition or active ingredient. Reforming reaction is partial combustion of methane or other hydrocarbon sources in the presence of water to form carbon monoxide and hydrogen, while oxidation reaction is the partial combustion of methane in oxygen to give carbon monoxide, carbon dioxide and hydrogen. On the other hand, carbon forming reaction is the reversible pyrolysis of methane or other hydrocarbon sources and disproportionation of carbon monoxide to carbon dioxide to form carbon and syngas.

Moreover, reports of current depletion of conventional fossil fuel reservoirs [3, 4] and increasing discoveries of heavy crude oil and bitumen deposits around the world [5, 6] has threatened global industrialization. However, this energy insecurity perceived in the near future could be averted with unconventional reservoirs upgrading which currently stands at 9.1 trillion barrels making it 70% of the world total oil resources [5].

Conversely, syngas is a promising fuel [7]. In the past it has been used to provide hydrogen for various industrial applications [8], and fuel sources in the case of fuel cells [9] and methanol synthesis [10]. In Fischer-Tropsch synthesis, it is used to manufacture liquid fuels from gas, coal or biomass [11]. Recently, it has found application as a direct fuel in hydrogen internal combustion engines for land and air transportations [12].

In this chapter we attempt to review the sustainable application of syngas in heavy crude oil and bitumen upgrading via water gas shift reaction. Various works on this area were critically discussed to ascertain the participation of syngas in the upgrading process via gas chromatography analysis of the gaseous product which shows high proportions of carbon dioxide and hydrogen when the starting materials are simply water in a neutral environment with a suitable catalyst and the heavy crude oil/bitumen hydrocarbon. Although, these hydrocarbons are non-renewable the upgrading method selected in this chapter is tenable, as a consequence the overall technology is partially sustainable.

Reforming reactions $CH_4 + H_2O \leftrightarrow CO + 3H_2$ $C_nH_m + mH_2O \leftrightarrow nCO + (n + \frac{1}{2}m)H_2$	+206 kJ/mol Endothermic	Steam methane reforming (SMR)
Oxidation reactions $CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2H_2$ $CH_4 + O_2 \rightarrow CO + H_2O + H_2$ $CH_4 + \frac{3}{2}O_2 \rightarrow CO + 2H_2O$ $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	-36 kJ/mol -278 kJ/mol -519 kJ/mol -802 kJ/mol	Partial combustion
Carbon forming reactions $CH_4 \leftrightarrow C + 2H_2$ $2CO \leftrightarrow C + CO_2$ $CO + H_2 \leftrightarrow C + H_2O$ $C_nH_m \leftrightarrow nC + \frac{1}{2}m H_2$	+75 kJ/mol -172 kJ/mol -131 kJ/mol Endothermic	Boudouard reaction

Table 1.
Reactions in syngas production.

2. Heavy oil upgrading

Heavy crude oil and bitumen upgrading technologies can be classified into; carbon rejection, hydrogen addition (hydrocracking) and separation processes [13, 14]. Hydrocracking is a process of upgrading heavy crude oil in the presence of hydrogen and a suitable catalyst, whereby the latter is usually dual functional with the hydrogenating and cracking sites, while the former inhibits secondary reactions that produce coke [15]. However, hydrocracking as simply defined above has been established to be the most suitable technology for heavy crude oil and bitumen upgrading [16]. Consequently, various methods abound for hydrocracking processes with distinct strategy along the lines of temperature and pressure operating conditions, type of reactors, composition and type of catalysts, and ultimately the methods of providing hydrogen.

Hydrogen can be supplied directly as a pure gas [17–20], produced in-situ from chemical compounds and biological species [21–24], or extracted from syngas process in-situ via water gas shift reaction [20, 25–28]. In the first case, a significant amount of hydrogen proceed to hydrogen sulfide (H_2S) [18, 20] and the process is over the odds [19]. The impediment of the second method is low conversion [22] and inability to operate at relatively higher reaction conditions due to biological species [23, 24]. However, supply of hydrogen via syngas is inexpensive [25], has high conversion rate [26–28] and the reaction could be operated between low water gas shift reaction (200–350°C) [28, 29] and high water gas shift reaction conditions (350–450°C) [20, 27]. In addition, higher upgrading has been reported with processes where hydrogen was obtained via syngas to pure hydrogen gas [26].

2.1 Catalytic reaction in neutral environment

In heavy crude oil and bitumen upgrading where the hydrogen is supplied from syngas, the source is usually from water in-situ [13] or introduced into the reactor alongside feedstock [20, 25–31]. Irrespective of the method of providing water, the reactor would be pressurized in a neutral environment, usually nitrogen to mimic reservoir conditions.

Fumoto et al. [32] studied the suppression of coke generation in upgrading of bitumen by examining the time factor (W/F) of the catalyst and mixture of steam and nitrogen as feedstock at 500°C and atmospheric pressure. Meanwhile, Chao et al. [33] developed a new type of difunctional catalyst in heavy oil upgrading. The starting materials include; 100 g of heavy crude oil and water in a designed mass ratio, catalyst and nitrogen gas at 240°C and 3 MPa. Similarly, the role of water in the redox reaction between bitumen and water in the presence of a suitable catalyst was studied by Dejhosseini et al. [25]. They observed that bitumen cracking was supported either through oxidation of active oxygen species generated from water or hydrogen via the redox (syngas) reaction (**Figure 1**).

2.2 Production of syngas

Syngas process follows a series of endothermic and exothermic reaction steps, subdivided into three major units (not in order of occurrence); reforming, oxidation and carbon forming reactions as shown in **Table 1** [34].

It is suitable to state here that only at temperatures above 700°C would the SMR dominate carbon formation reactions, also the other steps of syngas production are reversible reactions except oxidation reactions which only goes in the forward direction.

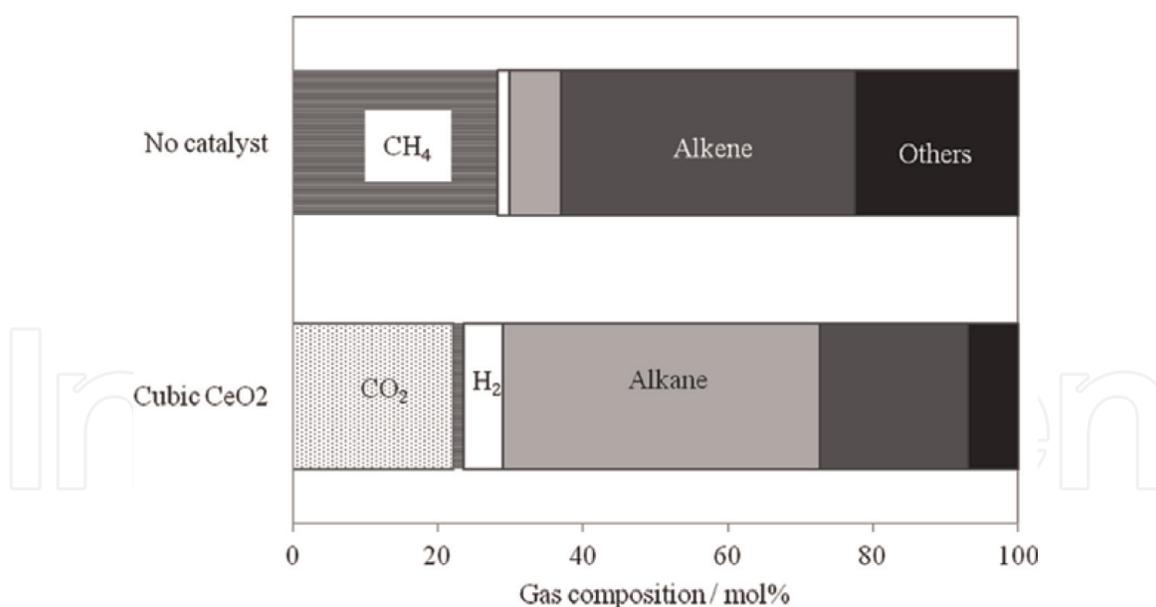


Figure 1.

Gas composition after the reaction of bitumen in presence and absence of cubic CeO₂ nanoparticles at 450°C in supercritical water [25].

To ascertain the process of syngas during hydrocracking reactions, researchers usually utilize gas chromatography to analyze the produced gas. Results obtained show that in the presence of water and a suitable catalyst, these gases contain a considerable amount of carbon dioxide, carbon monoxide and low quantity of hydrogen assuming majority have been consumed by free alkyl chain molecules to form light oils [20, 25].

Certainly, heavy crude oil or bitumen reactivity and hydrogen availability are the two major factors responsible for the extent of upgrading [35]. Accordingly, the latter is the bedrock of upcoming technologies since the former is inflexible. In other respect, syngas could directly be injected into the upgrading process with the intention that on contacting carbon monoxide with the catalyst additional hydrogen would be generated for the upgrading reaction [36]. Bitumen can also be upgraded in supercritical water, hydrogen and carbon dioxide mixtures with the hydrogen and carbon dioxide species produced via decomposition of a carboxylic acid in the presence of water [37].

GC-MS analysis of the produced gas after upgrading with and without catalysts in the presence of water was used to measure the extent of upgrading and participation of water gas shift reaction in the overall process. **Figure 2** displays the GC-MS chromatogram of upgrading of heavy crude oil in the presence of alkyl ester sulfonate copper catalyst and water, where (a) is without catalysts and (b) with catalysts [33]. The first peak is carbon dioxide with abundance almost twice as much with catalysts than without catalysts. Since carbon dioxide is a product of water gas shift reaction alongside hydrogen in 1:1 stoichiometric molar ratio, it is reasonable to conclude that syngas is involved in the catalytic upgrading of heavy oil in the presence of water actively reducing the viscosity by 90%.

Fumoto et al. [38] exploit syngas in the form of water gas shift reaction for oxidative cracking of residual oil to produce useful light hydrocarbon fuels. Analysis of the gaseous product of the cracking process depicts carbon dioxide predominates. In the experiment without catalysts, methane and other lower saturates and alkenes constituted the gaseous effluents. Active hydrogen and oxygen species were formed from water via syngas which are consumed in the process thereby producing excess carbon dioxide and hydrogen as shown in **Figure 3**. In a similar manner, Ajumobi et al. [39] analyzed the gaseous effluents of the upgrading of oil sand bitumen via

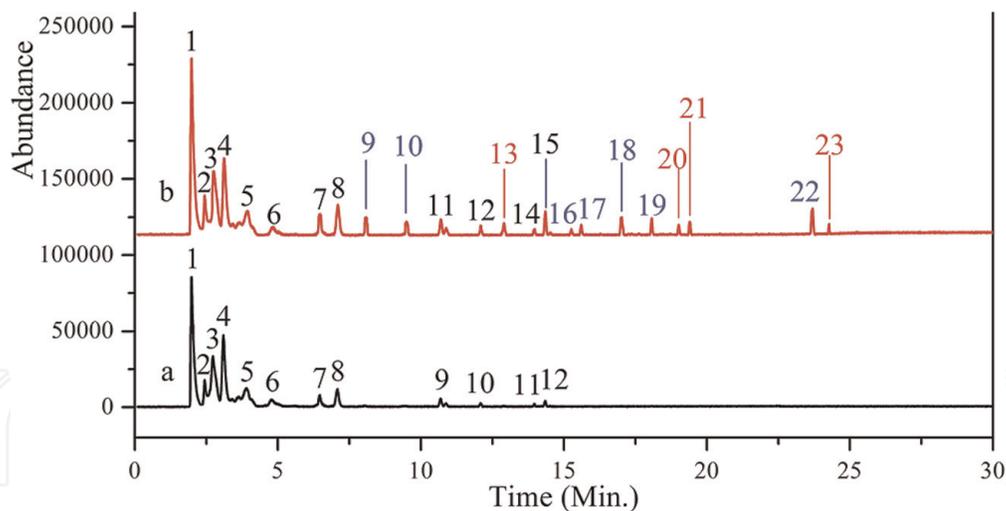


Figure 2.
 GC-MS spectra of the pyrolytic gas after reaction (a) without and (b) with the difunctional catalyst [33].

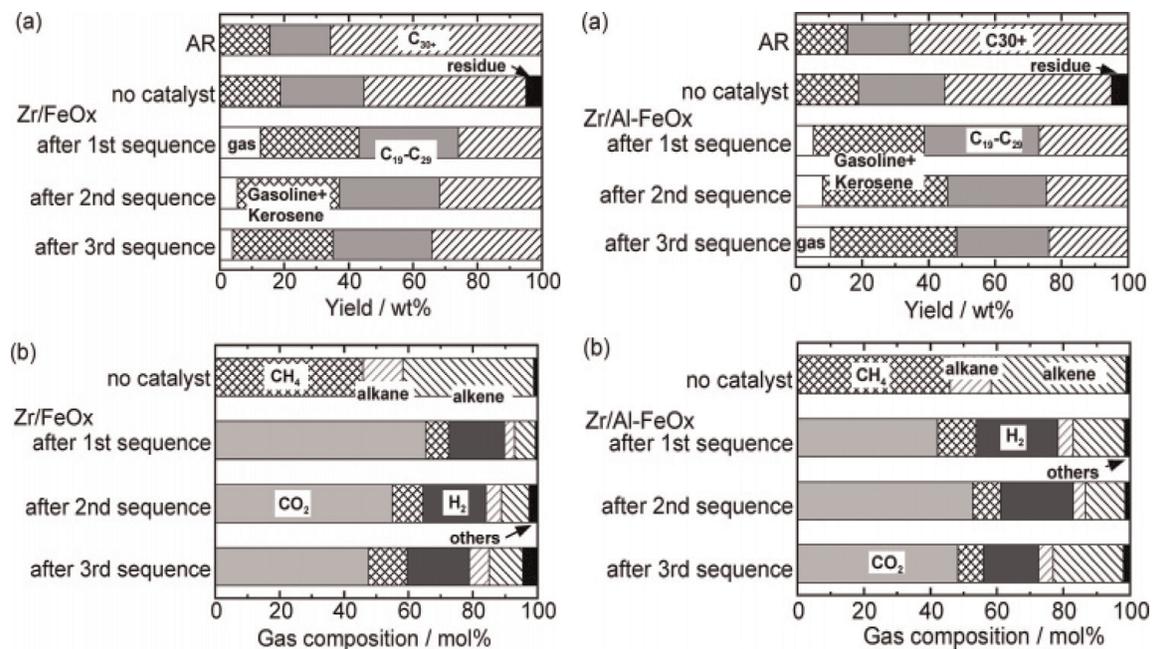


Figure 3.
 (a) Liquid product yield and (b) gas compositions after the sequence of the reaction of residual oils with steam over Zr/FeO_x and Zr/Al-FeO_x catalyst and regeneration [38].

ceria-based catalysts in steam environment and reported higher compositions of carbon dioxide and hydrogen in the experiments with catalysts as against that without catalyst resulting in higher light oil yields of approximately 60 mol% carbon. Therefore, it is evident from the foregoing that without the presence of a suitable catalyst to provide active hydrogen from water components the upgrading process would be impaired. Hosseinpour et al. [40] observed that the maltenes transforms to coke during vacuum residue upgrading in supercritical water.

3. Application of syngas

Syngas dates back to energy but over the years goes by different names depending on its starting material; producer gas, town gas, blue water gas, water gas, synthesis gas, syngas and so on. Earlier in this chapter it has been shown that water gas shift reaction is a pertinent step in syngas production.

Owing to its significance and age, extensive research has been dedicated to the study of syngas ranging from production to application. On the whole, syngas can be produced from gas, oil, coal or biomass via steam reforming, partial oxidation or gasification. The as-synthesized syngas can be applied in Fischer-Tropsch synthesis to produce synfuels, methanol synthesis to produce methanol or water gas shift reaction to produce hydrogen.

3.1 Syngas to synfuels

Liquid fuels can be manufactured from syngas with one of three processes; gas-to-liquids (GTL), coal-to-liquids (CTL), and biomass-to-liquids (BTL) via the Fischer-Tropsch synthesis [41]. The synthesis was developed in 1923 as a series of catalyzed chemical reactions which could be summarized to the basic reaction (Eq. 4),



with the liquid fuel hydrocarbon building from the methylene group attaching sequentially on a carbon chain. Although there have been extensive work on the Fischer-Tropsch synthesis, the reaction mechanism is still vague. Generally, the process requires a cobalt or iron catalyst [42, 43] to convert any carbonaceous raw material into synthetic natural gas, liquefied petroleum gas, light and heavy petroleum, middle distillate, kerosene, Diesel, and waxes [44, 45].

3.2 Syngas to methanol

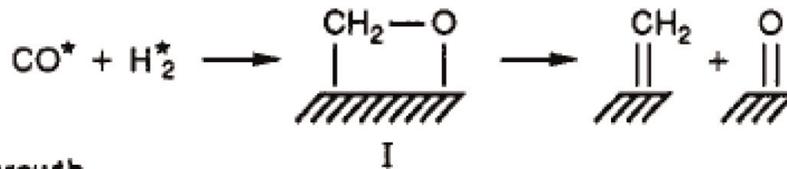
Methanol is an important industrial intermediate and doubles as a medium for hydrogen storage. The synthesis is as old as wood fires, as history tells that the methanol used in World War I was derived from destructive distillation of wood [46]. Unlike the Fischer-Tropsch synthesis, there is established reaction mechanism for catalytic production of methanol from syngas as far back as 1977, later modified by the same authors in 1991 [47]. In their scheme they considered the formation of surface species on the catalyst and production of ethanol as by-product. They further suggested that the chain addition of methylene group to the surface adsorbed aldehydes (species I–IV) are important steps as shown in **Figure 4**. In 2003, Reubroycharoen et al. [48] proposed a more simplified mechanism with Cu-based oxide catalyst using alcohol as catalytic solvent. They successfully produced methanol from syngas with a semi-batch autoclave reactor operating at 170°C and 50 bar reporting a one-pass yield of 47% and a selectivity of 98.9%.

3.3 Syngas to hydrogen

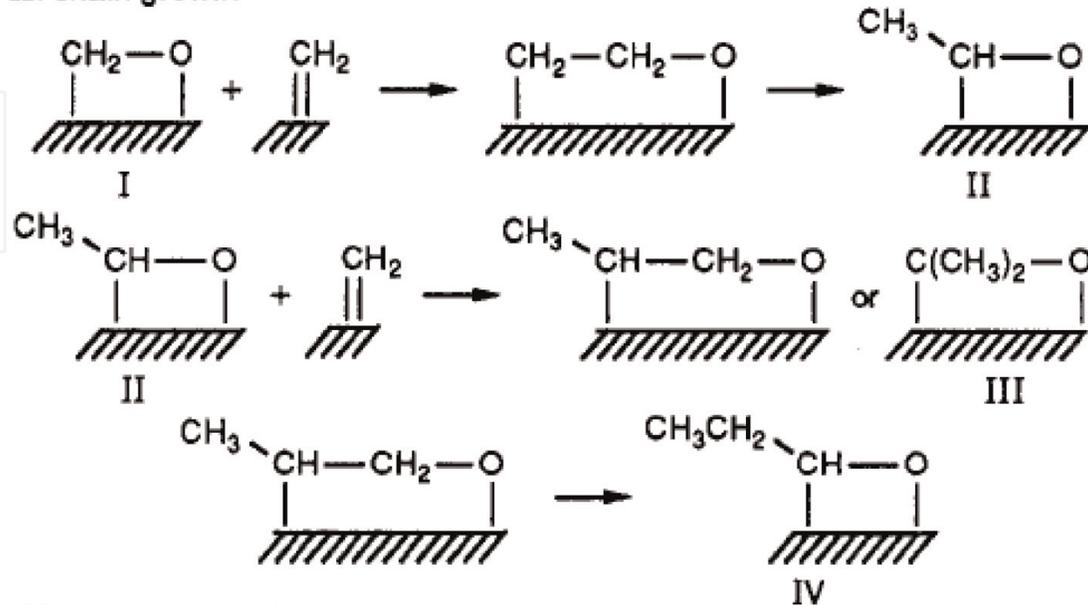
The importance and various application of hydrogen cannot be overemphasized. Hydrogen has found application as industrial chemical in manufacture of fertilizers [41], metal work [44], glass and steel production [46], and coolant in electricity generation [47]. However, its large scale application is still in the energy sector [49] where it is applied directly or indirectly. Direct application of hydrogen is in internal combustion engines [50] and fuel cells [51]. Indirectly hydrogen is used to produce liquid fuel [52], methanol [53], and upgrading of heavy crude oil and bitumen [54].

The best method of heavy crude oil and bitumen upgrading in line with sustainability is in-situ generation of hydrogen considering economic and environmental footprint [55–57]. Applications of syngas by way of water gas shift reaction have

I. chain initiation



II. chain growth



III. chain termination

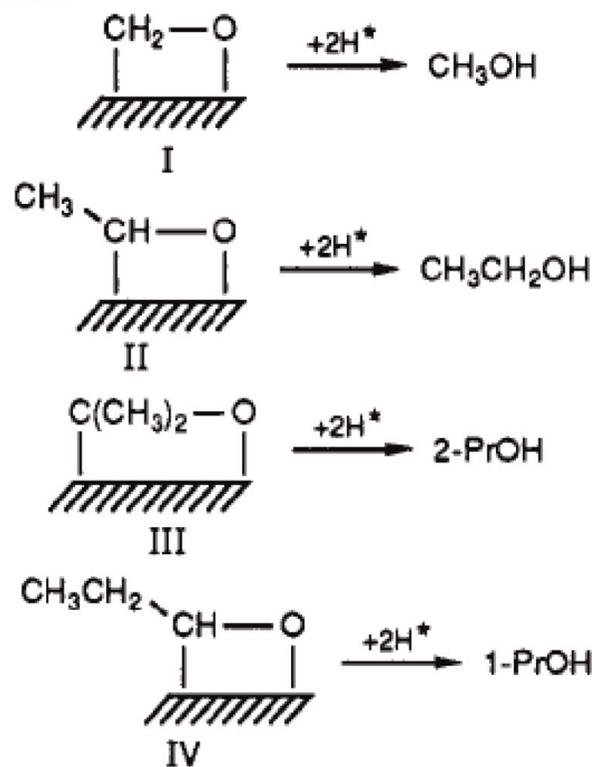


Figure 4.
 Reaction steps for methanol synthesis from syngas [47].

produced tremendous results in heavy oil upgrading. In the first place, sufficient reaction mechanisms have been used to explain the process [58, 59], also successful field tests have been conducted [60], and lastly there are ample reports of obtaining better upgrading when hydrogen is supplied via water gas shift reaction as against pure hydrogen gas [13, 27, 61].

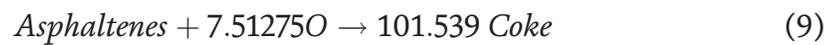
Kapadia et al. [62] studied the in-situ generation of hydrogen from bitumen gasification in the presence of methane via water gas shift reaction. They included

in their scheme; thermal cracking, low and high temperature oxidation reactions, coke gasification, water gas shift reaction, methanation, and hydrogen and carbon monoxide combustion reactions and solved the following elementary steps Eqs. (5)–(17) derived from various literatures [62, 63];

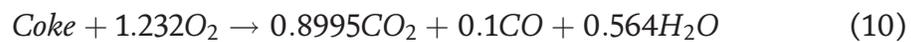
Thermal cracking reactions



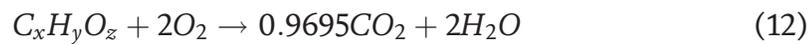
Low temperature oxidation reactions



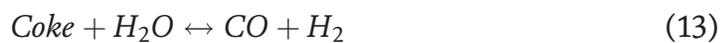
High temperature coke oxidation reaction



High temperature gas oxidation reactions



Hydrogen generation reactions



Hydrogen consumption reactions



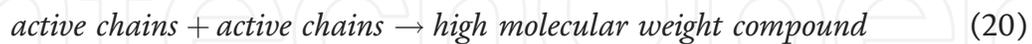
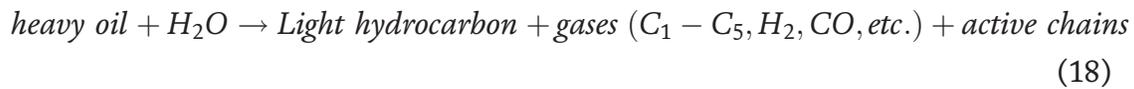
Carbon monoxide combustion reaction



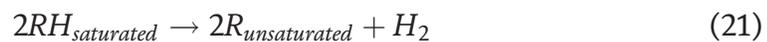
and successfully predicted hydrogen production, bitumen pyrolysis and aquathermolysis when compared with experimental data. They observed that at higher temperatures the mechanism favors coke gasification and water gas shift reaction resulting in high concentration of carbonaceous gases and ultimately hydrogen.

A comparable experimental investigation was made in the upgrading of heavy crude oil using Co-Mo/Al₂O₃ catalysts. On the one hand steam was supplied as feedstock and on the other hand pure nitrogen was used to pressurize the reactor to observe the effect of steam and ultimately water gas shift reaction [64]. Their results showed that 92% viscosity reduction was obtained in the steam environment as against 85% in nitrogen. The coke content of the product was also decreased to 11 wt% in steam as against 27 wt% obtained with nitrogen. This goes on to show that water gas shift reaction plays an important role in the catalytic upgrading of heavy

crude oil to produce required hydrogen needed to prevent the secondary reaction of the carbon-carbon bond scission products during cracking to coke. This hydrogen also come in play to reduce the recombination of active chains formed by cleavage of C–C, C–S, C–N, and C–O bonds to form large molecules [65]. They deduce a simple reaction steps to depict the effect of water Eqs (18)–(20).



An Agilent gas chromatograph refinery gas analyzer was used to determine the composition of the produced gases from the nitrogen feedstock and those of varying steam-oil ratio (SOR) as shown in **Table 2**. It could be observed that the total gas produced with nitrogen reaction 6.61142 vol% is twice that produced in the various SOR reactions 3.61152, 3.00644 and 3.64143 vol%. It is learnt that during heavy crude oil cracking, hydrogen is formed from subtraction of excited saturated to unsaturated hydrocarbons and C–H bond cleavage as shown in Eqs. (21)–(23).



Gas	No steam (vol%)	SOR (0.1) (vol%)	SOR (0.05) (vol%)	SOR (0.02) (vol%)
Methane	2.33	1.15	1.27	1.46
Hydrogen	2.4	1.37	1.1	1.41
Ethane	0.82	0.06	0.033	0.03
Carbon dioxide	0.03	0.07	0.064	0.054
Ethene	0.03	0.07	0.08	0.073
Propane	0.23	0.21	0.15	0.113
Propene	0.14	0.10	0.07	0.068
i-Butane	0.12	0.14	0.03	0.062
n-Butane	0.06	0.14	0.03	0.073
i-Butene	0.051	0.035	0.034	0.044
cis-2-Butene	0.00	0.037	0.029	0.038
trans-2-Butene	0.02	0.033	0.00	0.023
n-Pentane	0.19	0.11	0.064	0.11
i-Pentane	0.17	0.07	0.034	0.064
Carbon monoxide	0.02	0.016	0.018	0.019
Hydrogen sulfide	0.00042	0.00052	0.00044	0.00043
Total	6.61142	3.61152	3.00644	3.64143

Table 2. Produced gas composition during catalytic upgrading reaction in nitrogen atmosphere only and in combination with steam [64].

With the steam reaction having more advantage of generating extra hydrogen via water gas shift reaction, it is unexpected to record lower hydrogen composition compared to nitrogen environment. However, it is easy to perceive that the unaccounted hydrogen for the steam experiments have been consumed during hydrogenation, hydrodesulfurization and de-coking as reported earlier. On the contrary, one would expect that the high composition of hydrogen reported in the experiment without steam would increase the upgrading, lower coke formation or improve olefin saturation. Nevertheless, it has been reported that the proton formed via water gas shift reaction has higher hydrogenating reactivity than others [13].

Another observation in **Table 2** is the high volume of methane recorded in the reaction without steam. In the presence of water and a suitable catalyst, methane undergoes steam-methane reforming (SMR) to produce syngas according to Eq. (24).



In a bid to further explore the resourcefulness of syngas in hydrocracking of heavy crude oil and bitumen, hydrogenation could progress either through the forward water gas shift reaction (Eq. 3) or reverse water gas shift reaction (Eq. 25).

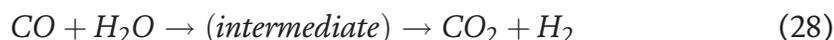


A comprehensive research structure was used to demonstrate this in hydrodesulfurization of dibenzothiophene using NiMo/Al₂O₃ catalysts at 673 K and 30 MPa [61]. Four different mixtures; hydrogen-water, carbon monoxide-water, carbon dioxide-hydrogen-water, and HCOOH-water were used as hydrogen sources, and conversion were obtained in the order; carbon monoxide-water, carbon dioxide-hydrogen-water, HCOOH-water and hydrogen-water. It would be observed that the carbon monoxide-water and carbon dioxide-hydrogen-water combinations are the forward and reverse water gas shift reactions respectively. Product analysis of the carbon dioxide-hydrogen-water mixture revealed trace amount of carbon monoxide a product of reverse water gas shift reaction (Eq. 25).

Basically, there are two mechanisms postulated for the water gas shift reaction; the regenerative mechanism and the associative mechanism. In the regenerative mechanism, the redox reaction on the surface of the catalysts is responsible for the hydrogen production [66]. It is proposed that the catalysts surface is oxidized by water to produce hydrogen followed by reduction of the surface to convert carbon monoxide to carbon dioxide as seen in Eqs. (26) and (27).



For the associative mechanism, an adsorption-desorption model was proposed which involves intermediate and eventual desorption to carbon dioxide and hydrogen (see Eq. 28).



4. Sustainability

Syngas is acclaimed to be the energy of the future [7]. Hydrogen on the other hand has found application as a direct fuel in hydrogen internal combustion engine,

an improvement from its initial application in fuel cells and energy storage. The sustainability of syngas as a fuel could be argued in accordance with its starting material, environmental footprint and economic implication. Interestingly, syngas can be produced from petroleum residua, coal, biomass and a number of opportunity fuels such as industrial and municipal wastes. The negative environmental impacts of these materials cannot be overstressed as much as the positive environmental impact of burning pure hydrogen coupled with growing technology of carbon capture, ultimately leading to the green technology of syngas as alternative fuel. However, the use of biomass and carbonaceous waste as feedstock would require tar removal [44], coupled with the fact that the reaction mechanism of the Fischer-Tropsch synthesis is still not well understood would negatively impact the economic implication of producing liquid fuel from syngas.

Alternatively, heavy crude oil and bitumen resources and technology for upgrading them is copious. Moreover, the literature is stacked with established reaction mechanisms for supplying hydrogen to aid hydrocracking via water gas shift reaction (or syngas). Although, they are finite non-renewable energy resources; their abundance makes them inexpensive, utilizing in-situ water gas shift reaction is economical and produce far less environmental footprint than supplying pure hydrogen, and their technology is comprehensible and accessible. In essence, syngas coupled with heavy crude oil and bitumen upgrading could provide near-term global energy independence, while facilitating the transition to a more sustainable syngas fuel.

5. Conclusion

Water gas shift reaction is an important step in the production of syngas. Interestingly, the sustainability of syngas span across the raw materials, process and application in fuel production as alternative to current and future energy demands. Worthy of note is its application in upgrading over 8 trillion barrels heavy crude oil and bitumen resources via water gas shift reaction to produce low molecular weight hydrocarbon separated into gases, liquefied petroleum gas (LPG), gasoline, naphtha, kerosene, diesel, gas oil, lubricating oil, greases and so on in a conventional refinery. For this purpose, hydrogen is produced in-situ from syngas with a suitable oxide catalysts and water from dehydrated or non-dehydrated crude. Upgrading via syngas gave lower viscosity and higher saturates. The process is also economically viable and environmentally friendly because of the absence of hydrogen gas in the feedstock and lower hydrogen sulfide in the gaseous product stream respectively. Although, heavy crude oil and bitumen are non-renewable fossil fuels, their abundant reserves and method of in-situ hydrogen generation during upgrading qualifies them as future alternative fuel and sustainable resource respectively.

Conflict of interest

The authors declare no conflict of interest.

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