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Synthesis Gas Purification

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Résumé — Purification des gaz de synthèse — Les procédés de synthèse de biocarburants par voie Fischer-Tropsch (FT), voies B-XTL, représentent des alternatives prometteuses pour la production d'énergie. Ces procédés permettent la conversion en carburants de synthèse de biomasse lignocellulosique, éventuellement mise en œuvre en mélange avec des charges fossiles telles que petcoke, charbons ou résidus sous vide. Pour ce faire, une étape de gazéification convertit la charge carbonée en un gaz de synthèse (mélange de CO et H₂), lequel, après ajustement du ratio H₂/CO et élimination du CO₂, subit ensuite la réaction de Fischer-Tropsch. Les gaz de synthèse contiennent cependant de nombreuses impuretés qui nécessitent d'être éliminées afin d'éviter l'empoisonnement des catalyseurs Fischer-Tropsch.

En raison de la grande variété de charges pouvant être mises en œuvre, la composition des gaz de synthèse est susceptible de subir d'importantes variations, en particulier de part la nature des impuretés (éléments, spéciation) présentes ainsi que leurs teneurs relatives. La composition des gaz de synthèse est également soumise à des spécifications extrêmement sévères en terme de pureté liées à l'importante sensibilité aux poisons des catalyseurs FT. Pour ces raisons, la purification des gaz de synthèse constitue un défi majeur pour le développement des procédés B-XTL.

Dans cet article, nous présentons les principaux enjeux liés à la purification des gaz de synthèse. Les différents types d'impuretés pouvant être présentes dans les gaz de synthèse sont présentées. L'influence de la nature de la charge, des technologies de gazéification ainsi que des conditions opératoires associées sur la nature des impuretés et leurs teneurs relatives est discutée. Une attention particulière est portée au devenir des composés soufrés, azotés, des halogènes, métaux lourds et métaux de transition. Les principales technologies de purification des gaz de synthèse (adsorption, absorption, réactions catalytiques, etc.) sont finalement décrites, ainsi que les défis associés.

Abstract — Synthesis Gas Purification — Fischer-Tropsch (FT) based B-XTL processes are attractive alternatives for future energy production. These processes aim at converting lignocellulosic biomass possibly in co-processing with petcoke, coal, or vacuum residues into synthetic biofuels. A gasification step converts the feed into a synthesis gas (CO and H₂ mixture), which undergoes the Fischer-Tropsch reaction after H₂/CO ratio adjustment and CO₂ removal. However synthesis gas also contains various impurities that must be removed in order to prevent Fischer-Tropsch catalyst poisoning.

Due to the large feedstocks variety that can be processed, significant variations of the composition of the synthesis gas are expected. Especially, this affects the nature of the impurities that are present (element, speciation), as well as their relative contents. Moreover, due to high FT catalyst sensitivity, severe syngas specifications regarding its purity are required. For these reasons, synthesis gas purification constitutes a major challenge for the development of B-XTL processes.

In this article, we focus on these major hurdles that have to be overcome. The different kinds of syngas impurities are presented. The influence of the nature of feedstocks, gasification technology and operating conditions on the type and content of impurities is discussed. Highlight is given on the fate of sulfur compounds, nitrogen compounds, halides, transition and heavy metals. Main synthesis gas purification technologies (based on adsorption, absorption, catalytic reactions, etc.) are finally described, as well as the related challenges.

INTRODUCTION

To protect the environment and conserve natural resources, a more diverse energy mix is essential, particularly in the transportation industry. As the only liquid fuels that can be used to supplement fossil based transportation fuels, biofuels play a major role in the diversification process.

First-generation biofuels, blended with conventional gasoline or Diesel, are available at the pump. They can be divided into two main categories: biodiesel, which is produced from a variety of oils, including rapeseed, sunflower and soybean, and blended with conventional Diesel, and ethanol, which is produced by fermenting sugars or starch and blended with gasoline [1, 2].

Some research is also currently focusing on the development of second-generation biofuels that can be made from non-edible, lignocellulosic materials derived from wood, straw, forest wastes, and dedicated crops. By using the non-edible part of plants, second-generation biofuels are expected to enable to meet growing biofuel needs without competing with food production. In addition, they can use raw materials that are in abundant supply and deliver an interesting environmental performance.

Two pathways are being explored: biochemical conversion and thermochemical conversion. Especially, as shown in Figure 1, thermochemical conversion consists in the gasification of carbonaceous feedstocks under partially oxidizing atmosphere into a synthesis gas (or syngas) composed of a CO-H₂ mixture [3]. After multiple gas conditioning steps aimed at reaching the required specifications (H₂/CO ratio adjustment and CO₂ removal) [4, 5], the syngas undergoes the FT reaction in order to produce synthetic liquid fuel [6-8]. However, synthesis gas also contains various impurities that must be removed in order to prevent FT catalyst poisoning [9-12].

A large variety of biomass feedstocks can be used in the gasification process, after a pretreatment (torrefaction)

aiming at increasing the biomass specific heat capacity and reducing biomass grinding energy [2, 13]. Various feedstocks can also be co-processed in the gasification unit in addition or replacement of biomass, such as coal or petcoke. As a consequence of the large feedstocks variety that can be processed, significant variations of the composition of the synthesis gas are expected. Especially, this affects the nature of the impurities that are present (element, speciation), as well as their relative contents. Moreover, due to high FT catalyst sensitivity, severe syngas specifications regarding its purity are required. For these reasons, synthesis gas purification constitutes a major challenge for the development of B-XTL processes (Biomass to Liquids, X = Coal, Petcoke).

In this article, we focus on these major hurdles that have to be overcome. The different kinds of feedstocks and syngas impurities are presented. The influence of the nature of feedstocks, gasification technology and operating conditions on the type and content of impurities is discussed. Highlight is given on the fate of sulfur compounds, nitrogen compounds, halides, transition and heavy metals. Main synthesis gas purification technologies (based on adsorption, absorption, catalytic reactions, etc.) are finally described, as well as the related challenges.

1 SYNTHESIS GAS COMPOSITION

Three main types of feedstock are usually considered for gasification: biomass, coal and petcoke alone or mixed in different proportions. Typical inorganic concentration of each kind of feedstock has been reviewed from bibliography data [14-23]. Main characteristics of various feedstocks (elemental composition) are reported in Table 1.

Biomass is characterized by a large variability of the dry ash (woody biomass ash content from 0.3 to 5 mass%, agricultural residue ash content up to 20 mass%) [22, 23]

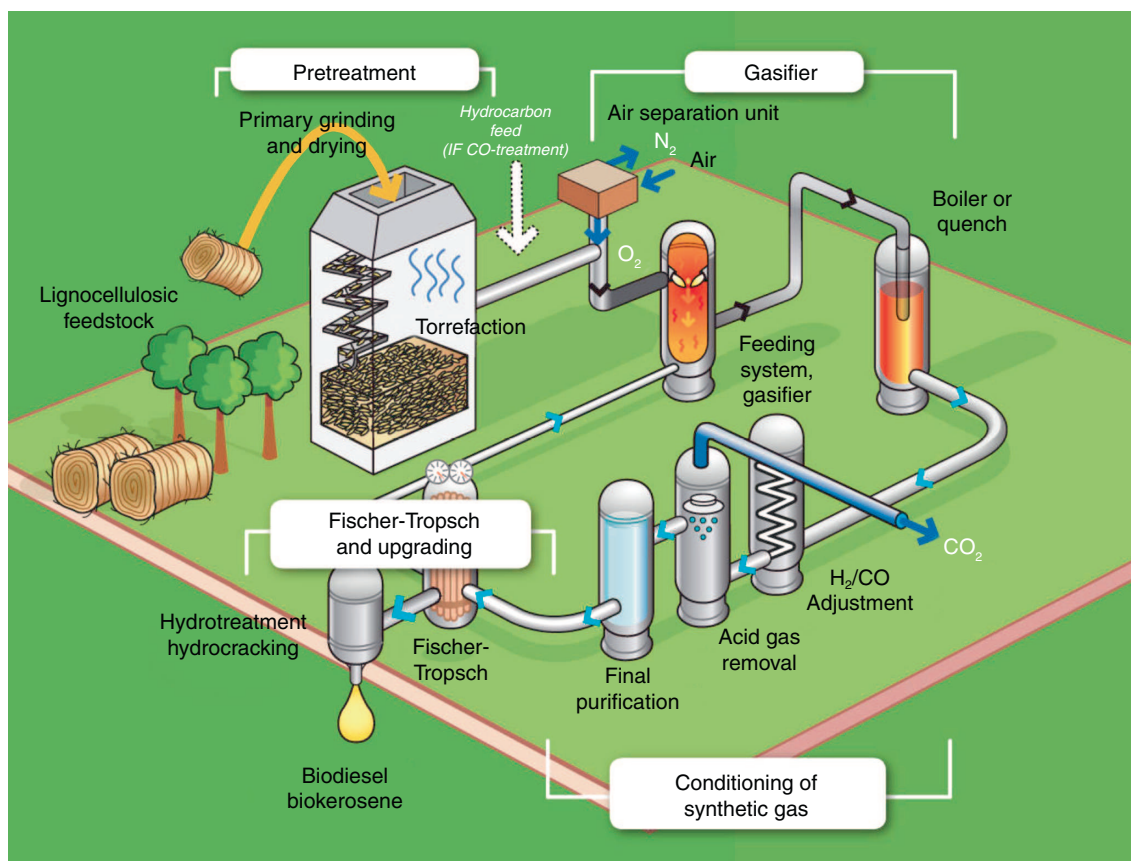


Figure 1

Schematic representation of the second-generation biofuels production chain from B-XTL thermochemical routes. (source: IFP Energies nouvelles).

and inorganic contents (Tab. 1). Woody biomasses have generally lower sulfur, phosphorus, nitrogen and chlorine contents than agricultural co-products and energy crops. Woody biomass exhibits mean sulfur content of 800 mass.ppm, whereas agricultural biomass sulfur content is generally higher (average of 1500 mass.ppm) [22]. Wood biomasses nitrogen and chlorine contents are respectively lower than 0.8 mass% and 340 mass.ppm, whereas agricultural biomass contains up to 2.1 mass% nitrogen for alfalfa, and much more chlorine with an average content of 2500 mass.ppm and values up to 6500 mass.ppm for corn, tall fescue or fiber sorghum [23].

Coals are characterized by a very large variability of dry ash from 1 to 50 mass% (depending on the coal). Volatile inorganic nitrogen and sulfur are high and in the same range for all coals: high nitrogen (above 1 mass%), high sulfur (0.3 to few mass%) and very low chlorine contents. Petcoke is characterized by the

lower dry ash (< 5 mass%) and chlorine (0.01 mass%) content but the higher sulfur (> 5 mass%) and nitrogen (> 1 mass%) contents of the three kinds of feedstock. Same main elements (> 100 mass.ppm) are present in biomass and coal, *i.e.* Al, Ca, Fe, K, Mg, Mn, Na, Si, Zn).

Coal contains more medium content (10 to 100 mass.ppm) elements than biomass (As, Cd, Co, Cr, Cu, Ti and V). Petcoke composition differs from coal and biomass regarding the presence of higher Ni, Sr and V contents. Main characteristic of coal and petcoke is the much lower chlorine content and higher sulfur content compared to biomass. This will affect the composition of the raw syngas, with respect to each compound.

1.1 Synthesis Gas Composition: Major Species

The synthesis gas produced by the gasification of carbonaceous feedstocks, such as biomass, petcoke and

TABLE 1

Composition ranges of biomass, petcoke and coal feedstocks. Biomasses considered in this table are wood, biodried wood, willow, railroad ties, verge grass, cacao shells

	Content (mass.ppm)			References
	Biomass	Coal	Petcoke	
Alkali metals				
Na	40-4 500	100-1 500	15-91	[18-20]
K	260-30 000	50-3 000		[18, 19]
Alkali earth metals				
Mg	200-5 400			[18]
Ca	2 000-18 500		5-127	[18, 20]
Sr	10-60		0-70 000	[18, 21]
Ba	4-160			[18]
Halogens				
F	10-130	100		[15, 18]
Cl	160-8 600	300		[15, 18]
Br		25		[15]
Transition metals				
Ti	0-260	500		[15, 18]
V	0.3-22	1-100	5-1 000	[15, 16, 18-21]
Cr	1-160	0.5-60	2	[15, 18-20]
Mn	10-1 000	5-300		[18, 19]
Fe	70-4 500		0-260	[16, 18, 20, 21]
Co	0.1-5.6	0.5-20		[15, 18, 19]
Ni	0.5-650	0.5-100	200-490	[15, 16, 18-21]
Cu	0.5-50	5-60		[18, 19]
Mo	0.6-2.4			[18]
Zn	5-260	1-1 000		[15, 18, 19]
Cd	0.2-2.4	0.05-10		[15, 18]
Hg	0.01-0.9	0.02-3		[15, 18, 19]
Post transition metals				
Al	60-6 900		3-131	[18, 20]
Sn	1-12	5-10		[15, 18, 19]
Pb	1-250	1-300		[15, 18, 19]
Metalloids				
B	3-45	5-100		[15, 18, 19]

(continued)

TABLE 1 (continued)

	Content (mass.ppm)			References
	Biomass	Coal	Petcoke	
Si	600-47 000		7-472	[18, 20, 21]
As	0.2-6.9	0.5-10		[15, 18, 19]
Sb	0.6-2.6	1		[15, 18, 19]
Other non metals				
N	2 700-33 900	9 600-12 000	10 500-33 900	[14, 15, 18, 20]
P	53-3 700	50		[15, 18]
S	430-2 500	3 000-9 500	5 000-62 000	[14-16, 18, 20]
Se	0.2-1.2	0.2-3		[15, 18, 19]
Te	0.9-1.2			[18]

coal, consists mainly in H_2 , CO , CO_2 and H_2O . Syngas composition varies as a function of the nature of feedstocks and gasification technology [3, 24-27].

Syngas composition can be adjusted to the needs of the FT synthesis, that requires specific H_2/CO ratio. For this purpose, the syngas usually undergoes a water gas shift conditioning step (CO conversion with steam into H_2 and CO_2) [5]. CO_2 inert gas removal is then achieved through an acid-gas removal step, performed using solvent scrubbing systems [4]. Different types of the existing processes are described in Section 2.1.

Some other chemical species are found in synthesis gases, resulting from compounds initially present in the primary feedstock.

1.2 Sulfur Compounds

Sulfur compounds should be present in the synthesis gas as H_2S and COS , also depending on the gasification process operating conditions [3, 11]. The presence of organic species such as mercaptans and thiophenic compounds in synthesis gases obtained from coal gasification is also reported [3]. It however may occur for gasification processes operating at low temperature (fixed or fluidized bed). In gasification processes operating at temperature higher than $1\ 400^\circ C$ such as entrained flow reactor, sulfur is only present in the synthesis gas as H_2S and COS , and no organic sulfur compounds should be found downstream according to thermodynamic calculations. Biomass feedstocks generally have a much lower sulfur content than fossil feedstocks (coal, petcoke) [3, 11, 28, 29]. Syngas sulfur content may thus vary from hundreds to thousands of ppm as a function of the feedstock.

1.3 Nitrogen Compounds

Nitrogen species present in the feedstocks are converted into HCN and NH_3 in the gasification process. According to literature, the NH_3/HCN ratio depends on many parameters [30-33], such as the nature of feedstocks (that may contain nitrogen compounds with different speciation), operating conditions of the gasification process such as pressure and temperature, gasification process technology (fixed bed, fluidized bed, entrained flow reactor). Nitrogen feedstock contents may vary from 0.1 to 3.3 mass% [11, 14, 15, 18], which affect accordingly the resulting nitrogen syngas contents after the gasification step [34].

It is worth noticing that in the gasification process, the formation of HCN should be predominant from aromatic nitrogen compounds found in fossil feedstocks, whereas combustion of aminoacids and other nitrogen species usually present in biomass predominantly leads to the formation of NH_3 [3, 11, 31]. Syngas HCN contents may vary from a few mol.ppm to hundreds of mol.ppm, and NH_3 contents from a few mol.ppm to 14 000 mol.ppm [3, 11]. Other nitrogen compounds might also be present in synthesis gases such as isocyanic acid $HNCO$, and nitrogen oxides NO_x , also depending on the gasification operating conditions and technology [3, 11].

1.4 Halogen

The chlorine content in biomass may vary from 0.01 to 0.9 mass% [22]. Chlorine species in the syngas are most of the time identified but rarely quantified. Chlorine species such as HCl , KCl and $NaCl$ are formed during the

gasification of chlorine containing feedstocks [18, 35-38]. Chlorine compounds could also react with NH_3 in the raw gas to form NH_4Cl [3]. Gas composition is reported to vary with the gasification temperature and the source of feedstock [25, 37].

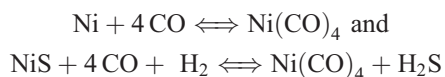
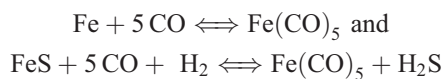
1.5 Metals

Chemical compounds containing metal atoms, such as mercury, iron or nickel, can be found as impurities in synthesis gases.

Usually mercury in hydrocarbons can be found as elemental (Hg^0), oxidized (Hg^{2+}), and particle-bounded (HgP) [39]. Mercury contents in petcoke and coal may vary from 50 to 500 mass.ppb (dry basis) [40, 41]. Numerous works have also investigated the amount of mercury in biomass feedstocks; according to studies, mercury biomass content may vary from 1 to 40 mass.ppb (dry basis) [42-47]. Overall, the content of mercury is less important in biomass feedstocks than in hydrocarbons and is often below the detection limit. However, some feedstocks can contain up to 40 mass.ppb of mercury similar to the averaged content found in petcoke for instance.

Several works have addressed the form of mercury from coal combustion and gasification and the general conclusions may possibly be extended to biomass feedstocks. The gasification operating at very high temperatures will transform the different species of mercury in elemental mercury Hg^0 . For instance, Lu *et al.* [48] showed that the reducing environment of syngas is not favorable for Hg oxidation *via* gas phase reactions alone and that mostly elemental mercury is expected to remain in the syngas from coal gasification.

Metal carbonyls are common impurities of CO containing gases. Metal carbonyls, mainly iron carbonyl $\text{Fe}(\text{CO})_5$ and nickel carbonyl $\text{Ni}(\text{CO})_4$ (other carbonyls, such as cobalt compounds, being solid in the operating conditions of XTL chain), are gaseous toxic compounds formed during the cooling of raw synthesis gases [3]. They result from the reaction between carbon monoxide CO and metals (or metal containing compounds such as sulfides). The reaction leading to the formation of metal carbonyls (also noted $\text{Me}(\text{CO})_x$ in the following) are shown hereafter:



Equilibrium data were reported by Higman and van der Burgt [3]. From these data, it can be seen that

metal carbonyls formation increases with increasing pressure (and/or increasing CO partial pressure) and decreasing temperature. Moreover, $\text{Ni}(\text{CO})_4$ formation takes place at significantly higher temperatures than $\text{Fe}(\text{CO})_5$ formation. Formation of metal carbonyls is also more favored from metals (*i.e.* Fe and Ni) than from the corresponding sulfides. Consequently, the presence of H_2S in the syngas may hinder the formation of gaseous $\text{Me}(\text{CO})_x$ (or favor their decomposition into corresponding metal sulfides).

Therefore, metal carbonyls formation may take place at low temperature ($T < \sim 300^\circ\text{C}$), and as a consequence not in the gasifier. $\text{Me}(\text{CO})_x$ formation could be favored from metal containing ashes downstream gasification units [49]. In addition to the primary source of $\text{Me}(\text{CO})_x$ in the raw syngas cooling, $\text{Me}(\text{CO})_x$ are also reported to form through contact between syngas and steel from process equipments (pipelines, process units, heat exchangers, etc.) [50, 51].

1.6 Other Elements

Many other elements might be present in raw syngas after feedstocks gasification. Some thermodynamic calculations aimed at determining trace elements in raw syngas from coal [15, 52, 53] biomass [54] or petcoke [14, 16] gasification have shown that many more compounds have to be considered. It results from these studies that some alkali metals (Na, K), metals (As, Zn, in addition to Hg, Fe, Ni), and heteroelements (B, Se) might be present in the gaseous phase. Zn, Na, and K are however expected to condense as sulfides or chlorides particles at gasification outlet during syngas cooling, and form aerosols. The future of As and Se compounds however requires further investigations.

1.7 Challenges

Due to the large variety of feedstocks that can be processed, and also as a function of the gasification technologies used, a wide range of synthesis gases with fluctuating composition has to be considered. Some heteroelements and inorganics compounds present in the syngas are expected to affect XTL process operation and performances.

Chemical species condensing at gasifier outlet, which form aerosols in the raw syngas (such as KCl , NaCl , ZnS , HgS), are not expected to be an issue, as these species will be removed by filtration or by water wash cleaning units. Some elements such as F, Cl and B, highly soluble in water, are not expected to cross water wash cleaning units (if 100% efficient). Oxidized mercury may also form within the gas stream by combination

TABLE 2
Gas purification requirement for Fischer-Tropsch application. Target levels for major contaminants

	Turk <i>et al.</i> (2001) [12] Newby <i>et al.</i> (2001) [58]	Tijmensen <i>et al.</i> (2002) [55]	Boerrigter <i>et al.</i> (2003) [59]
H ₂ S	Total sulfur < 0.06 mol.ppm	H ₂ S + COS < 0.01 ppm*	H ₂ S + COS + CS ₂ < 1 mol.ppm
COS			
HCN	< 0.01 mol.ppm	HCN + NH ₃ < 0.02 ppm*	HCN + NH ₃ < 1 mol.ppm
NH ₃	< 10 mol.ppm		
NO _x	< 0.1 mol.ppm	–	–
Halides	Total halides < 0.01 mol.ppm	HCl < 0.01 ppm*	HF + HCl + HBr < 0.01 mol.ppm
Alkalis	–	< 0.01 ppm*	< 0.01 mol.ppm

* Mass. or mol.ppm not specified.

with impurities like Cl, and should be therefore also removed in water wash sections, but it is very likely that a large amount of elemental mercury still remains in the gas phase [48].

Compounds such as sulfur, nitrogen, halogens, and metal species remaining in the gaseous phase are expected to highly affect XTL process operation.

Indeed, if not totally removed by water wash cleaning units, the presence of chlorine species (such as HCl) may cause serious problems along the B-XTL chain: especially downstream corrosion, fouling and Fischer-Tropsch catalyst poisoning [12, 55].

Though the mercury syngas levels are expected to be rather low, the impact on the industrial equipment and human health can be serious. For instance, mercury has a strong ability to form amalgams with Al-based cryogenic exchanger leading to corrosion issues and potential industrial disaster like the one encountered in Skikda, Algeria [56]. In addition, mercury is harmful for human health and numerous incentives have been issued to control and limit its emissions from anthropogenic sources [56, 57]. The incorporation of a purification step is therefore necessary to remove elemental mercury from the syngas.

Me(CO)_x presence strongly depends on the process scheme, that will affect syngas temperature, pressure and composition (CO partial pressure being a key parameter), whose variations may lead to Me(CO)_x formation or decomposition. Metal carbonyls decomposition in units located downstream the gasifier results in the deposition of Ni or Fe metal particles, or eventually of sulfide particles if H₂S is present. The solid deposition may have various possible consequences, as a function of the position where the decomposition takes place. For example in catalytic processes, a consequence can be a modification of solid catalytic properties, such as a loss

of activity or the appearance of side reactions (such as coke formation through the Boudouard reaction, FT or methanation reactions) [3, 49].

Finally, among the impurities present in syngas, small amount of sulfur and nitrogen compounds are expected whatever the kind of feedstock (fossil or biomass), which are known to be severe poisons for FT catalysts [9, 10, 12, 55].

As a consequence, the strategy for syngas treatment and impurities management should be reminded according to each process configuration chosen. Specific impurity removal processes are therefore needed to reach low specifications required for the FT application (*Tab. 2*).

2 PURIFICATION PROCESSES

2.1 Acid Gas Removal (AGR) Processes

2.1.1 Main Existing Technologies for H₂S and CO₂ Removal

Acid gases in a gasification process typically consist of H₂S, COS, and CO₂. Current processes of removing these gases from the raw syngas typically involve counter-current absorption with a regenerative solvent, in an absorber column. The solvent type processes can be divided into three types [4]:

- chemical solvents such as alkanolamines based solvents;
- physical solvents using for instance methanol (Rectisol process) or mixture of dimethyl ethers of polyethylene glycol (Selexol process);
- hybrid solvents (chemical and physical solvents) such as alkanolamine (*e.g.* DIPA) + sulfolane (Sulfinol process).

The main challenge of these technologies is to reduce the sulfur content to as low as possible and as

economically as possible. Indeed, whatever the choice of the acid gas removal technology, a final purification step is required to achieve complete sulfur removal and to reach the low sulfur content specifications required for FT synthesis catalysts.

Chemical solvents include primary, secondary and tertiary amines as listed in Table 3. Through acid-base reactions, aqueous solutions of basic alkanolamines remove acid gases by forming weak chemical bonds with dissolved acid gases in the absorber according to following reactions:



TABLE 3
Common alkanolamine solvents

Solvent		Type of amine
Monoethanolamine	MEA	Primary
Diglycolamine	DGA	Primary
Diethanolamine	DEA	Secondary
Diisopropanolamine	DIPA	Secondary
Triethanolamine	TEA	Tertiary
Methyldiethanolamine	MDEA	Tertiary

The bonds are broken by heat in the regenerator to release the acid gases and regenerate the solvent for reuse. Chemical solvent absorption processes normally operate slightly above ambient temperature.

A simplified process flow scheme representing a typical amine AGR unit is shown in Figure 2.

The main advantages of amine-based processes are a low capital and solvent cost, and a low co-absorption of syngas main components. The main disadvantages of amine based processes results from high heat requirements for solvent regeneration due to high heat of reaction, amine solvent degradation and corrosion, and a poor COS removal.

In physical solvents the dominant driving force is the acid gas partial pressure difference between the gas phase and the liquid phase. Therefore, the higher the pressure is the better the absorption is. Physical solvent absorption processes normally operate at cryogenic temperatures.

The main advantages of a physical solvent [60] lie in its high selectivity for H₂S and COS absorption towards CO₂ absorption, high loadings reachable for high acid gas partial pressures resulting in low circulating rates, good solvent stability, low heat requirements for solvent regeneration as it can be partly performed by pressure letdown. Main disadvantages of a physical solvent [61] are related to complex process scheme resulting in high

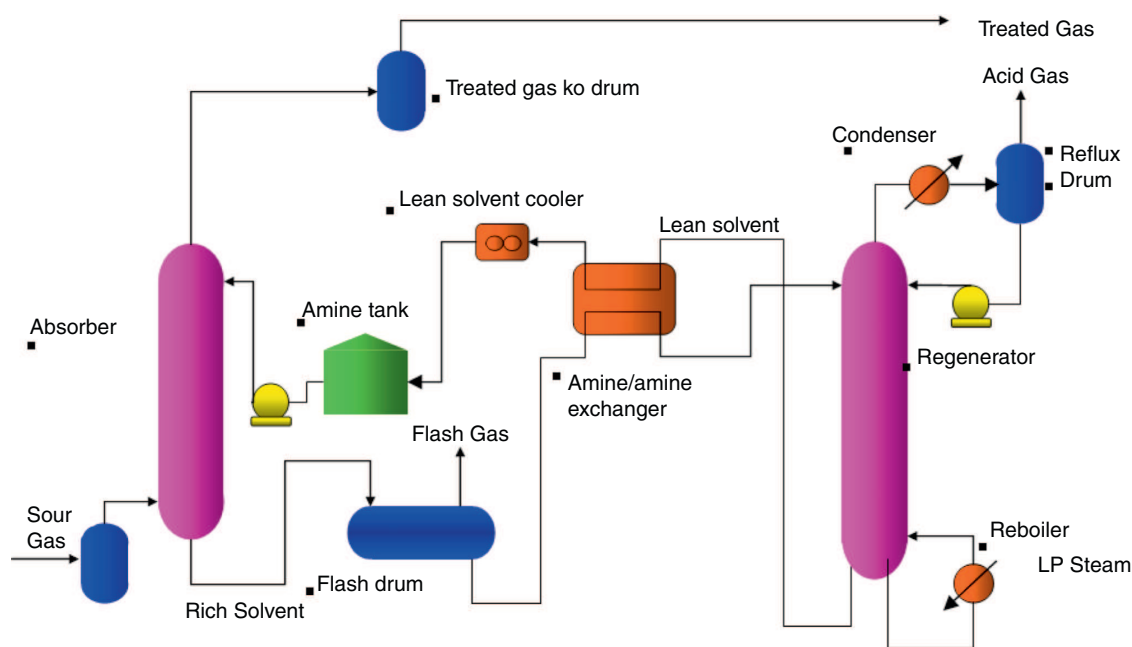


Figure 2

Basic process flow diagram of an amine gas treating unit.

capital costs, and low operating temperature requiring refrigeration facilities and leading to thermal performances losses and high operating costs.

However, these technologies do not allow to achieve complete H₂S removal [4], as expected H₂S syngas content at AGR systems outlet (in the range 0.1-1 mol.ppm) remains higher than sulfur syngas content tolerated at FT inlet [9].

2.1.2 COS Removal

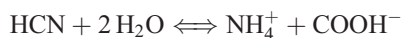
As MDEA does not combine chemically with COS, only a physical COS removal can be performed with this amine requiring high circulation rates of solvent. New formulated MDEA solvents are reported to achieve high degree of COS removal. However, for syngas that contains appreciable quantities of COS, a removal of COS prior to the amine wash unit is usually necessary [60].

According to Korens *et al.* [60], who also provide absorption coefficient of various gas in methanol (physical solvent), COS has a very high solubility similar to the one of H₂S. Therefore H₂S and COS are removed simultaneously from the syngas in Rectisol unit and no COS hydrolysis is required upstream the acid gas removal unit [62].

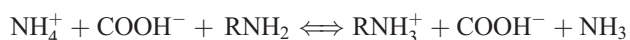
The Selexol process can be configured in different ways depending on the requirements of H₂S towards CO₂ selectivity and depth of sulfur removal. However Selexol process presents a relatively poor selectivity between COS and CO₂ and a COS hydrolysis unit can be used upstream the Selexol wash if an acid gas rich in H₂S is required and a high level of COS removal is foreseen [60].

2.1.3 Efficiency of Absorption Processes on the Removal of Other Compounds

In amine process, hydrogen cyanide (HCN) reacts with water to form a formate anion and an ammonium cation according to:



The ammonia is stripped in the regenerator column leading to the protonation of the amine and the formation of amine formate which is a non regenerable heat stable salt [63].



Therefore, the presence of HCN in the syngas can cause the formation of heat-stable degradation compounds. A prior removal of HCN could be a preferable option.

In the case of Rectisol process, HCN will be removed from the syngas in a particular section of the Rectisol absorber column and it will be removed from the loaded methanol in a dedicated HCN separation column. A partition wall column can also advantageously used according to *Linde* for HCN separation [62].

Unlike HCN, ammonia (NH₃) does not lead to heat-stable salts formation and can be easily removed from the amine loop by purging the regenerator reflux drum [64]. In Rectisol process NH₃ can form ammoniumsulfide with H₂S that can result in a pollution of the product and the off gas and it can also form ammoniumcarbamate with CO₂ that can cause plugging of equipment. Therefore NH₃ has to be removed upstream of the acid gas removal unit, a good process is a simple water wash at countercurrent in an absorption column [62].

Strong acids like HCl react with the amine to form heat-stable degradation compounds (heat stable amine salts) that cannot be regenerated in the stripper. Generally, soda ash is added into the solution to neutralize the heat-stable compounds. Once concentration of these compounds reaches about 4 mass%, then the solution is reclaimed [65].

As HCl is highly soluble in cold methanol (data for 0°C) it may be assumed that Rectisol process will remove it at least partially [66]. However, FT specifications may not be reached.

2.2 Trace Contaminants Removal

Due to high FT catalyst sensitivity, high syngas purity levels are required that cannot be achieved with usual solvent based processes. Indeed, trace contaminants are remaining in the syngas after acid-gas removal processes and water scrubbing systems usually employed. The presence of contaminants as traces and their related deep removal processes are well documented for sulfur and nitrogen compounds or for mercury for example.

To ensure a deep removal of impurities, gas treatment processes based on physical adsorption, chemical adsorption or chemical reaction (solid absorption) onto a solid carrier bed are used.

In physical adsorption or physisorption, there is no chemical reaction between the solid and the molecules presents in the fluid. It occurs when the solid – gas interactions are stronger than the interaction in the gas itself. Physisorption is an exothermic process and occurs rapidly beginning by a monolayer and continuing in some cases by multi-layer formation. The adsorbate molecule is being held to the adsorbent *via* weak intermolecular attractions. Some of these processes, such as molecular

sieve dryers or Pressure Swing Adsorption (PSA), allow *in situ* regeneration of the bed. However, because of the physisorption interactions between impurities to be removed and the solid surface, they are thus not selective processes. These processes are also operated at low temperature (below 50°C).

In chemical adsorption or chemisorption, the molecule of the fluid reacts chemically with the solid. This reaction is generally slow and irreversible. It is usually accompanied by heat release and takes place at elevated temperatures. The adsorbate is strongly and irreversibly bonded to the adsorbent *via* chemical transformations. Separation processes based on chemisorption reaction are usually highly selective.

Other purification processes lie in chemical reaction between the gaseous compound to be removed and the solid used in the trapping media. These reactions entail bulk transformations of the solid, through chemisorption and solid-state diffusion mechanism. This kind of reactions is also generally slow and irreversible, and highly selective.

Some trace contaminants removal processes of interest for syngas purification applications are discussed hereafter.

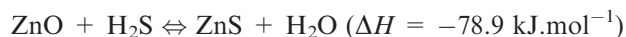
2.2.1 H₂S Removal

Materials used for selective H₂S removal processes based are metal oxides or metal compounds able to react with H₂S to form the corresponding metal sulfides (which results in solid bulk phase transformation). Most common metal oxides used for this application are zinc oxide, copper oxide (and/or copper), manganese oxide, nickel oxide (and/or nickel), iron oxide, lead oxide. Corresponding sulfidation reactions are thermodynamically very favored, as reported by Westmoreland and Harrison [67]. This results in a high selectivity toward H₂S removal. Sulfidation mechanisms and kinetics are reported for various metal oxides, as *e.g.* for ZnO for which abundant literature can be found. The sulfidation profile of ZnO pellets has been modeled according to shrinking core type mechanisms [68-70]. Studies on ZnO crystals sulfidation show outward growth of ZnS phase, with Zn diffusion through the resulting sulfide layer according to Kirkendall effect [71-73].

Zinc oxide is indeed one of the most widely used H₂S trapping media, as less side reactions are expected compared to other oxides, and because of its lower cost. Efficiency of ZnO for H₂S removal is very high [3], but its performance for trapping other sulfur compounds is limited (COS, RSH) [74, 75]. According to the literature [4], these compounds should be thus removed or converted

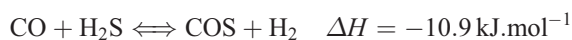
into H₂S upstream the ZnO guard bed. For the removal of traces of COS and organic sulfur, a layer of Cu-ZnO may be put at the bottom of the ZnO bed.

Hydrogen sulfide reacts with zinc oxide following the next reaction:



Being exothermic, the reaction is favored at low temperature. However, the process is generally carried out at high temperature to increase the reaction rate (generally between 100 and 350°C, maximum at 500°C). Theoretical maximum sulfur loading on pure ZnO is 39.5 mass% corresponding to the complete conversion of ZnO into ZnS. In general, the achieved capacity is near 25 mass% [76]. The sulfur removal rate is also depending on the characteristics of the sorbent: its textural properties, porosity and specific surface area [68, 70, 77, 78]. Moreover, the presence of H₂O, CO and CO₂ in the gas may influence the absorption of H₂S on ZnO:

- given the equilibrium reaction, presence of H₂O in the gas may affect the desulfurization performance of the trap [61, 76]. However, for temperature lower than 300°C, this is expected to show little impact on S removal;
- competitive adsorption between CO₂ and H₂S is reported to impact S trapping. Moreover, CO₂ and CO may react with H₂S to form COS, which is not efficiently adsorbed on the ZnO trap [61]. Formation of COS is favored either at high or low temperature depending on the reactant. However, the occurrence of those reactions will depend on H₂O or H₂ content in the syngas.



Some side reactions are reported in presence of H₂ and/or CO, and as a function of operating conditions. ZnO reduction into volatile Zn_(g) is reported to occur for ZnO from 500°C [79, 80]. This has led to the development of reduction resistant ZnO based trapping media (such as zinc titanate materials) for high temperature applications. Water gas shift reactions and methanol synthesis might occur on Cu/ZnO based sorbents, as they present similarities with catalysts used for these purposes [3, 5, 61, 81, 82]. Nickel based sorbents are not preferred for syngas purification applications due to a risk of nickel carbonyl formation.

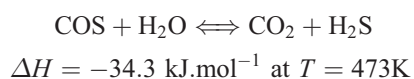
2.2.2. COS Removal

Existing technologies for COS removal based on adsorption and catalytic processes are reviewed in this section.

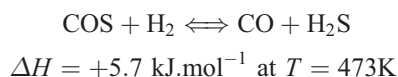
A review of some other existing processes for specific COS removal is also available in literature [83].

As COS molecule exhibits a relatively poor acidity and limited polarity, its reactivity is limited compared to CO₂. As a consequence, COS adsorption processes are not numerous, and *a priori* not advantageous. Few studies are however reported upon activated carbons impregnated with copper or iron salts [84], or upon metal hydroxides [85, 86]. Some commercial solutions are available when the feedstocks to be treated do not contain water and/or CO₂.

COS can also undergo hydrogenation and hydrolysis reactions, that may be catalytically favored. The COS hydrolysis reaction can be written as follows:



The COS hydrogenation reaction is endothermic and thermodynamically less favored:



The COS hydrolysis is therefore thermodynamically highly favored at low temperature, in opposition to the hydrogenation reaction (or sour gas shift reaction) whose equilibrium constant is weaker. The most employed strategy is thus to favor the COS hydrolysis in presence of a catalyst to improve the reaction kinetic. For this purpose, most studied catalysts in the literature are metal oxides such as TiO₂, Al₂O₃, ZnO and ZrO₂ [87, 88]. Especially, catalyst activity seems to be related to catalyst surface basicity [89, 90]. However, although ZnO is also known for its basic surface properties, controversial results can be found about this material, as for example according to Aboulayt *et al.* [89] who report results showing no activity of ZnO toward COS hydrolysis reaction.

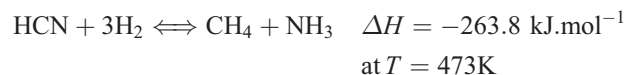
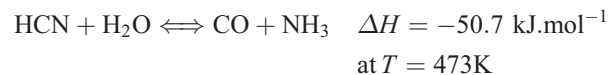
Alumina and TiO₂ catalysts, such as those used as catalysts in Claus processes, are also used to remove COS. Considering the activation energy, gamma alumina materials might be more active than TiO₂ materials [89, 91], and should thus favor COS hydrolysis from lower temperature ($T < 200^\circ\text{C}$). However, some experimental observations show the opposite; water, which is necessary to the reaction, can adsorb on catalyst surface and inhibit the catalytic activity. Alumina materials, that exhibit relatively high hydrophilic properties, seem to be more affected than TiO₂ based materials. Therefore, under operating conditions close to industrial conditions, TiO₂ based catalysts seem to be more active than

alumina catalysts. For example, this has been reported in a comparative study on commercial catalysts based on alumina (Kaiser-201, *Kaiser Aluminum and Chemicals*) and titania (CRS31, *Axens*) [91, 92]. Concerning any kind of catalyst, the specific surface area is a key parameter, COS conversion rate being favored when catalyst surface increases [88].

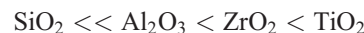
2.2.3 HCN Removal

A variety of activated carbons seems to be commercially available to adsorb HCN. These materials do not seem to have industrial applications for gas treatment (*e.g.* in refinery, etc.), but were studied for applications as filter in gas masks for air purification. The use of impregnated carbons with transition metals such as Cu, Zn, Ag, Co, Mo, and Cr is reported [93, 94]. HCN adsorption in NaX zeolites has also been studied [95], and on mesoporous silica impregnated with metallic ions [96].

HCN can undergo hydrolysis and hydrogenation reactions, that can be respectively written as follows:



Catalysts for HCN hydrolysis are reported to be very similar to those used for COS hydrolysis [87], allowing concomitant COS and HCN removal. Increasing activity of the following oxides towards HCN hydrolysis is reported to be:



2.2.4 HCl Removal

Although water wash cleaning unit and AGR will ensure a partial removal of HCl, the gas purity will probably not be sufficient to protect FT catalyst if no additional Cl guard bed is put after the AGR section. Chloride guard beds are typically configured as single-bed. They are non-regenerative units, which provide a service life from six months to several years [97]. These traps are sized based upon adsorbent chloride capacity, process stream and desired life cycle. Typically, adsorbent chloride capacities in gas phase applications vary from 10 to 30 mass%. For the trapping of HCl on adsorbents, two types of adsorption mechanisms exist as shown by reactions below: either physisorption or both physisorption and chemisorption mechanisms (*Tab. 4*).

TABLE 4

$M_xO_y + \text{HCl} \rightarrow M_xO_{y-1} - \text{O} - \text{HCl}$ (with $M = \text{Al, Si}$)	Physisorption
$2 \text{HCl} + M_2\text{O} \rightarrow 2 \text{MCl} + \text{H}_2\text{O}$ (with $M = \text{Na}$)	Chemisorption
$2 \text{HCl} + \text{MO} \rightarrow \text{MCl}_2 + \text{H}_2\text{O}$ (with $M = \text{Ca, Mg, Zn}$)	

Activated aluminas and molecular sieves were commonly used in the past for chloride removal through physisorption. In general, adsorbents based solely on physical adsorption do not generally perform well for the chloride trap application because their chloride loading capacities are too low (5 to 10 mass%). In consequence, promoters like alkaline and alkaline earth metal oxides have been added to improve their capacities.

The promoters used are essentially sodium oxide and calcium oxide. They may be added in various concentrations: typically no more than 14% to keep the mechanical integrity of the final product [97, 98]. HCl adsorption on promoted aluminas may occur *via* physisorption and chemisorption. However, super-promoted aluminas (showing the highest content of promoter) have been designed to work mainly by the chemisorption mechanism. These materials show a larger chloride removal capacity than promoted aluminas (up to 24 mass%), which is essentially linked to the amount of promoter introduced.

Bulk oxides (CaO, MgO and ZnO) can also be used as Cl traps. Zn-based products are the most common. Alumina is sometimes added in these materials to insure their physical integrity and strength [99]. In this class of chloride guard bed, HCl reacts directly with the reactive phases of the guard bed to form a salt. Performances of this type of absorbent are based not only on the chemical composition but also on the dispersion of the active agents and on the pore structure of the particles. Capacities up to 30 mass% have been reported for laboratory tests but are rarely confirmed in actual plant [98]. The mechanical resistance of saturated basic oxides is an important parameter to consider. Indeed, the absorption of large quantities of chloride on basic oxides significantly modifies the chemical composition of the solid, which might lead to a weakening of its mechanical properties.

Temperature may influence the Cl pick up. For materials taking advantage of both physical and chemical adsorption mechanisms (promoted aluminas), higher temperatures will favor chemisorption over physisorption while lower temperatures will favor physisorption over chemisorption. Increase of temperature may be

required to avoid competitive adsorption (with S species for example). For ZnO bulk oxide, temperature has to be chosen with care as this material is also known as a sulfur sorbent (competitive adsorption): formation of the sulfided phase is more favored thermodynamically over the chloride phase above 150°C. A temperature below 150°C is thus preferred for Cl removal on ZnO materials. The total amount of chloride retained on the bed is also influenced by the flow rate [99].

2.2.5 Hg Removal

The most efficient technology for mercury removal lies in trapping media used as guard bed where mercury reacts to form a stable non-hazardous compound (chemisorption of solid bulk phase transformation). Mercury removal systems in syngas must operate under reducing conditions (*i.e.* H₂). Most of these solids contain an active phase usually made of sulfur based compounds and mercury reacts with sulfur as the gas flows through the guard bed to form solid-state mercuric sulfide (HgS) also known as cinnabar or metacinnabar. Other sorbents use active phases like silver, which may form amalgam with mercury. After the active phase is exhausted, the spent adsorbent is shipped to a hazardous chemicals disposal site.

Trapping media are used under two forms. Either solid particles of active phase (bulk material) are mixed with a solid used as a binder [100, 101], or the active phase is deposited within the porous network of a solid support (*e.g.* activated carbon, alumina, zeolites, etc.) through impregnation methods (supported materials) [102].

Mercury trapping media are predominantly composed of active phases deposited in a porous support, which chemically react with mercury to form cinnabar or amalgams. Among the active phases, elemental sulfur reacts with mercury through a redox reaction in which mercury is oxidized and sulfur is reduced ($\text{Hg} + \text{S} \rightarrow \text{HgS}$). This active phase is mostly dedicated to dry gas streams purification as sulfur is soluble in contact with liquid hydrocarbon which may decrease the guard bed lifetime. Elemental sulfur is often deposited on activated carbons [103, 104]. Sulfided metals *e.g.* copper sulfide (CuS) or silver sulfide (Ag₂S) are alternative to sulfur sorbents as mercury can reduce the metal sulfide (*e.g.* $\text{Hg} + 2 \text{CuS} \rightarrow \text{Cu}_2\text{S} + \text{HgS}$) or can form amalgams with the metal ($\text{Hg} + 2 \text{Ag}_2\text{S} \rightarrow \text{Ag}_2\text{Hg} + \text{Ag}_2\text{HgS}_2$). Metal sulfides are often deposited on alumina support [105], and are more suited to moist feeds or liquid hydrocarbons as metal sulfides are less sensitive to water or liquid hydrocarbon than elemental sulfur. Metal Oxide (*e.g.* copper oxide CuO) can also be used as a precursor of sulfided

metal (e.g. CuS) and sulfided *in situ* if the gas stream contains H₂S in the required amount ($\text{Hg} + 2 \text{CuO} + 2 \text{H}_2\text{S} \rightarrow \text{Cu}_2\text{S} + \text{HgS} + 2 \text{H}_2\text{O}$). However the conditions of this *in situ* sulfidation are not optimized and can lead to the formation of undesired species (e.g. Cu₂S). An *ex-situ* pre-sulfidation is usually preferred as the conditions can be more precisely controlled. Some metals (e.g. Ag) can selectively capture mercury by an amalgamation process (for Ag: $\text{Hg} + 2 \text{Ag}^+ \rightarrow 2 \text{Ag} + \text{Hg}^{2+}$, and $\text{Hg}^{2+} + \text{Hg} \rightarrow \text{Hg}_2^{2+}$). Silver is often exchanged on zeolites, which serve as dual role to dehydrate and to remove mercury. Mercury is then released as mercury vapor upon heating in the regeneration cycle and the released mercury is then treated with a conventional mercury removal guard bed [106].

However, these commonly used active phases can undergo side reactions with other syngas components. Side reactions with H₂ or CO with active phase such as CuS or elemental sulfur are thermodynamically favored, but their relative kinetics towards HgS formation reaction are unknown. These side reactions should be avoided as it might lead to chemical species which are not reactive with Hg (e.g. leading to formation of reduced metal sulfide Cu₂S, and/or of H₂S, COS). The occurrence of side reactions may thus lead to decreased performance of trapping media, depending on the relative kinetics associated to the formation of each species.

In addition to side reactions, capillary condensation could be an important issue to the performance of supported active phases. Indeed, solids containing mesopores or micropores can be prone to the formation of liquid filled cavities in the porous network creating an additional mass transfer resistance to the diffusion of mercury within the support. The gas then usually bypasses the guard bed and mercury is no longer adsorbed in the trapping media resulting in an untreated syngas. Activated carbons and zeolites are particularly prone to capillary condensation due to large microporous volumes whereas aluminas are usually mostly mesoporous and can avoid this technical problem. Bulk phase trapping media can also be prone to capillary condensation depending on the solid textural properties.

Trapping media are also usually operated at temperatures above 25°C to enhance the reaction kinetic between mercury and the active phase. However, possible side reactions can also be possibly favored by increasing the temperature. In addition, trapping media are usually not operated above 150°C to avoid a costly heating of the gas. Stability problems of some active phases can also occur as for instance elemental sulfur melts above 115°C. The optimized operating temperature will therefore depends on the choice of the technical solution, specifically

to the nature of the active phase and the potential solid support.

2.2.6 Metal Carbonyls Removal

Some zeolites and activated carbons are reported to adsorb metal carbonyls, and might be used for industrial applications. Regarding zeolites, choice of the structure is determined by Ni(CO)₄ and Fe(CO)₅ molecules sizes (respective kinetic diameter of 6.7 Å and 7.0 Å) [107, 108], which impose minimum pore sizes. The most studied zeolites are faujasites, with pores sizes around 7 to 9 Å as a function of cations in the structure. Adsorption seems to be not favored on zeolites such as silicalite and mordenite (lower pore size), in opposition to faujasite, TMA-omega (MAZ) and Linde L (LTL) [107].

Two relevant studies regarding gas purification are available. In the first one [109], five adsorbents that can be used in a TSA process have been compared. Results show that activated carbon (BPL carbon Calgon, 1 100 m².g⁻¹) and HY zeolite (LZY-72 Linde, 900 m².g⁻¹) exhibit the higher sorption capacities (sorption capacity related to materials specific surface areas), and that the presence of CO₂ in the gas highly decreases sorption capacities. Metal carbonyl sorption is also shown to be favored when temperature decreases (from 38 to 22°C). However, the formation of pyrophoric iron particles after sorbent regeneration is problematic for a sorbent use at industrial scale (used sorbent unloading, and possible exothermic side reactions during sorbent operation).

In a second work [110], the abilities of various zeolites to adsorb metal carbonyls have been compared, in a synthesis gas and in presence of compounds that may affect metal carbonyls adsorption (H₂S, H₂O and CO₂). This study shows that sorption capacities depend mainly on materials microporosity (pore size and volume), with optimal sorption capacity for pore size between 7 and 8 Å. It is shown that the use of faujasite with high Si/Al ratio (dealuminated zeolites) seems adapted for metal carbonyls removal in a syngas containing water and eventually H₂S. Presence of CO₂ also negatively affects the metal carbonyl sorption capacity. The use of activated carbon might be also possible, but no information on water influence on metal carbonyls adsorption seems available in literature.

3 DISCUSSION

In addition to the purification steps, raw synthesis gases have to undergo multiple conditioning steps to reach

Fischer-Tropsch requirements. These conditioning steps aim at:

- adjusting the H₂/CO ratio through a catalytic Water Gas Shift (WGS) section. Part of CO contained in the syngas stream is converted into H₂ (through the reaction $\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$) [5] to reach H₂/CO FT specification (around a value of 2) [3, 111], whereas the value is generally lower than 1 in raw syngas, and may vary depending on gasification feeds;
- removing inert CO₂ through an Acid Gas Removal process (AGR) using regenerable solvents (*Sect. 2.1*).

Water Gas Shift can be conducted on a raw syngas stream, in the presence of important amount of H₂S; this step is also qualified in this case of Sour Water Gas Shift (SWGS) [5]. SWGS catalysts used are then H₂S resistant materials (*e.g.* CoMoS over alumina supports). Water Gas Shift can also be carried out downstream the AGR section after major impurity removal, and relatively deep H₂S elimination. WGS catalysts used in this case are sulfur sensitive materials such as Cu/ZnO (low temperature shift) or iron oxides (high temperature shift).

As for Water Gas Shift, the selection of the Acid Gas Removal process used for CO₂ and bulk H₂S removal (*Sect. 2.1*) mainly results from technological choices based on technical constraints (raw gas flow rate to be treated, purity required downstream AGR process, need for selective CO₂ and H₂S removal, process integration in an existing site, etc.), and process economics (capital expenditures, operating expenditures) [4].

Therefore, global synthesis gas purification philosophy will thus vary and have to be optimized as a function of previous technological choices and resulting technical constraints on the purification section (nature and relative contents of impurities to be removed upstream and/or downstream AGR section, upstream and/or downstream WGS section, processes integration, etc.).

Synthesis gas purification for Fischer-Tropsch synthesis therefore involves multiple steps and processes, which sequencing has to be optimized in order to favor process scheme efficiency to reach drastic syngas composition requirements, and B-XTL chain efficiency. The technology, economics, and global process efficiency have indeed to be considered and optimized, as the cost associated to the purification section may represent a significant part in the whole process chain.

The number of operations for syngas conditioning should be therefore as low as possible, and process scheme should be considered to avoid as much as possible gas cooling and reheat that might be required for each process operation. Syngas cleaning should not be performed by considering each impurity separately, but as a whole.

The co-treatment of wide range of biomass and fossil feedstocks will result in important variations of synthesis

gas composition. Consequently, the whole purification process scheme should be adapted to the treatment of broad range of impurities. As discussed, some impurities are well identified such as sulfur and nitrogen compounds. However other volatile chemical species might be encountered in synthesis gases, such as for instance arsenic or selenium compounds [112, 113], or metal carbonyls. Synthesis gas expected contents are for instance not well documented, as well as the impact of some impurities on a B-XTL chain, and further experiments on demonstration plant should provide relevant data. As a consequence, trace contaminants analysis (element speciation, detection and quantification) is also a challenge, to determine the nature of the chemical compounds present in the synthesis gas.

CONCLUSIONS

The large variety of feedstocks that can be processed in a B-XTL process induces the production of syngas with fluctuating composition. Some impurities in the syngas, coming from the feedstocks or equipment, are identified to affect B-XTL process operation and performances (including Fischer-Tropsch catalyst poisoning). These are mainly H₂S, COS, HCN, NH₃, HCl, Hg and metal carbonyls. A multi-step purification of the syngas is thus required, to ensure a deep removal of trace contaminants remaining in the syngas downstream acid gas removal section.

Acid gas removal processes are used to reduce H₂S content in the syngas and possibly COS. The choice of a technology is linked to the economics, composition of the syngas (selectivity required towards COS and presence of detrimental compounds), capacity, operating conditions, etc. Trace contaminants removal is then usually performed on solid carriers by means of physisorption, chemisorption or chemical reactions. Specific impurity removal processes are therefore needed to reach low specifications required for the Fischer-Tropsch application.

In a B-XTL process, challenges linked to the syngas purification are multiple. Mainly, the sequence of the purification sections has to be optimized to reach the drastic syngas composition required for the use of Fischer-Tropsch catalysts, to avoid side reactions on some traps, and to minimize the impact of the purification section upon the whole process chain efficiency.

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