

EuroBioRef

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Executive Summary

The syntheses of various compounds like higher alcohols, hydrogen peroxide (H_2O_2) and methylmercaptanes (MeSH) from the producer gas demand the cleaning of the syngas from various components that are considered harmful for the processes. Furthermore, gas cleaning is also required when syngas is used for power or heat production. All partners involved were contacted in order to collect any data available on the purity levels of the syngas required. Depending on the process, the content of sulfur (with the exception of MeSH synthesis), alkali, nitrogen and halogen species, tars, particles and water content must be controlled and reduced to the specified limits.

Available techniques on the gas cleaning are the POX unit of DTI and the purification catalysts of Haldor Topsoe. Furthermore, design of a gas cleaning system using activated carbons (commercial and new provided from WP4) will be attempted by CERTH

1. Introduction

The syntheses of various compounds like higher alcohols, hydrogen peroxide (H₂O₂) and methylmercaptanes (MeSH) from the producer gas demand the cleaning of the syngas from various compounds. The aim of the current deliverable report is to give preliminary information on the required level of purity of the derived syngas for each synthesis process as well as for its use for power production. All partners involved were contacted in order to collect any data available. This information will be the basis for the design and implementation of the gas cleaning system.

2. Specifications for the syngas requirements

2.1 Higher Alcohols Synthesis (HAS)

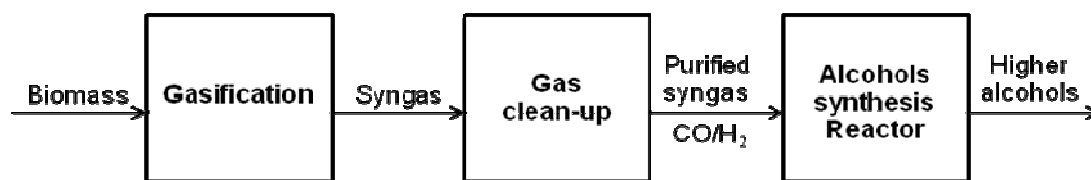


Figure 1: Synthesis of higher alcohols from syngas

Carbon monoxide and hydrogen from the producer gas are used for the synthesis of higher alcohols (Fig. 1). Employed heterogeneous catalysts in the process can be classified in three main categories:

- (a) Alkali-promoted Cu/ZnO-based modified methanol catalysts
- (b) Promoted Co or Fe catalysts supported on SiO₂ or Al₂O₃ modified Fischer-Tropsch catalysts
- (c) Alkali-promoted Mo-based materials

Both Cu-based and MoS₂-based catalysts will be used in two separate processes. A high temperature range, between 250-350 °C is desired while pressure should be between 30-80 bars both for a Cu-based and MoS₂-based catalysts.

The nature of the catalytic material and the chosen process obviously affects the maximum acceptable concentration of impurities in syngas. The above-listed impurity concentrations refer to either general limits reported in literature for higher alcohol synthesis (HAS) or limits specific to a certain catalytic system as described in detail below:

Tar content: A tar content of less than 0.1 mg/Nm³ for modified methanol and Fischer-Tropsch catalysts has been reported[1].

Sulfur species: 0,1 ppmv and 60 ppb [2,3] for the modified methanol and Fischer-Tropsch catalysts, respectively. Sulfide-based catalysts, such as MoS₂, do not have the strict sulfur clean up requirements of the other catalysts. In fact, these materials may require relatively high levels of sulfur (100 ppmv) [4,5] in the syngas in order to operate more efficiently. Studies have shown that COS does not cause any deactivation over a concentration range of 0.6-9 ppm [3].

Halogen species: The limits on HCl content in order to avoid catalyst poisoning are more severe than those for H₂S and range in the order of 1 ppb [6]. According to another source, halide levels in syngas should be less than 10 ppb [7].

Nitrogen: The referenced nitrogen levels reported are 10 ppmv NH₃ [1,3], 0.1 ppmv NO_x [3] and 10 ppb HCN [8] for alcohols.

Heavy metals: Heavy metals (As, Se, Hg) must be removed to parts per billion (ppb) levels prior to the synthesis reactor to prevent catalyst poisoning [9].

Alkali species: Alkali metals do not seem to pose any serious threat to the HAS catalysts as most of the reported active and selective HAS materials are alkali promoted. According to a literature report, alkalis should not be avoided as they increase the production of higher alcohols [3].

Other impurities: Other gas phase poisons in syngas that need to be avoided are metal carbonyls, particularly Ni and Fe carbonyls as they affect the selectivity of the catalysts in HAS. Metal carbonyl concentrations should be below 5 ppb [10]. Moreover, another poison to be avoided is P [3].

Water and CO₂ content: Very little information is available on the effect of CO₂ and water on higher alcohol synthesis catalysts. Controversial information is reported in literature, especially in the case of the CO₂ effect. Some catalysts are reported to require low levels of CO₂ and increased yields to higher alcohols have been recorded for 4-6% CO₂ in the feed [11]. MoS₂-based catalysts seem to tolerate relatively higher CO₂ levels than the other catalyst families (7%) [5]. However, the presence of CO₂ in the feed can also cause the formation of greater amounts of water via the reverse water-gas shift reaction and can poison the catalyst surface due to competitive adsorption [9]. No consensus has been reached concerning the influence of these two species. Moreover, no specific limits are reported for either water or CO₂.

2.2 H₂O₂ synthesis

Two different processes are followed for synthesis of H₂O₂, the anthraquinone process and the direct process (Fig. 2). The temperature ranges between 0-45°C at pressures of 3-6 bars for the anthraquinone process and 40-60 °C for the direct one, with pressure depending on the technology used, varying between 10-300 bars.

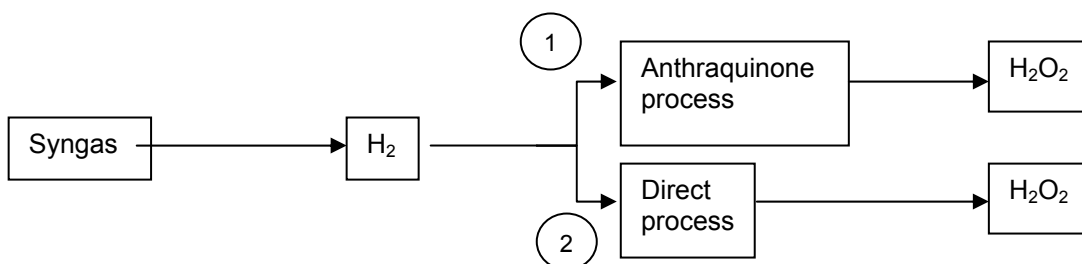


Figure 2: Synthesis of H₂O₂ from syngas.

The concentrations of several harmful to the processes components are given below:

Tar content: No tars should stay in the syngas for the syntheses.

Sulfur species: Less than 1ppm for both processes.

Halogen species: Cl₂ content must be less than 1ppm, or NaCl less than 60ppm.

Nitrogen: Requirements for H₂O₂ synthesis are not known. Estimations are that HCN as a possible catalyst poison should be less than 1 ppm, and that NH₃ has a negative influence at around 50ppm, and should be kept lower than 10ppm.

Heavy metals: Heavy metals (As, Se, Hg) must be removed to less than 0.01ppm as they are severe catalyst deactivators.

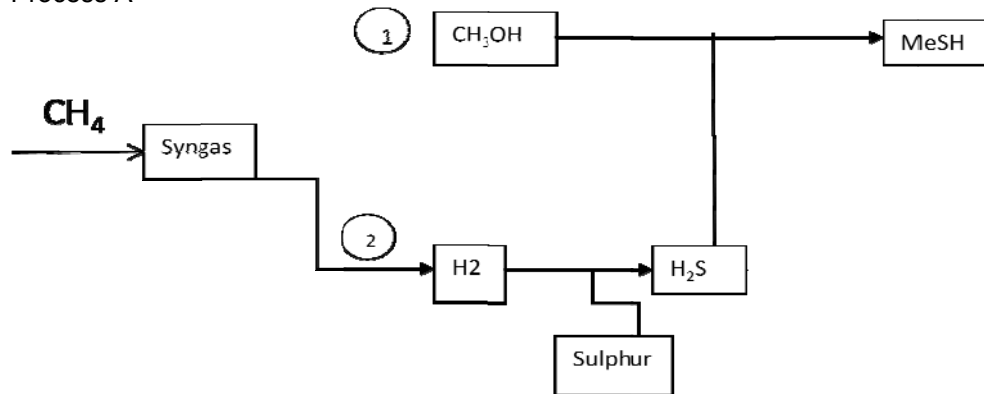
Alkali species: The influence of alkali species is not known, although specifications require NaCl content less than 60ppm in the anthraquinone process.

CO and CO₂: CO is a known deactivator and a concentration of less than 1ppm is acceptable in both processes. CO₂ is an H₂O₂ decomposition accelerator and could also affect the catalyst, thus should be kept below 1ppm.

Water content: Below saturation

2.3 MeSH synthesis

Process A



Process B

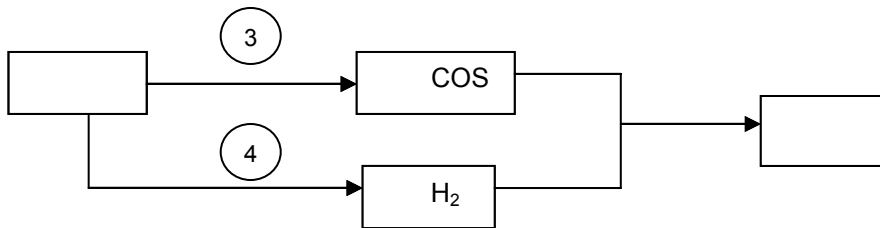


Figure 3: Two processes of MeSH synthesis from syngas.

Two methods are followed for the production of MeSH, one with the addition of methanol (CH_3OH) and one with an H_2/CO ratio equal to or above two (Fig. 3). Temperature should be kept below 400°C whereas pressure must be less than 25 bars for the first process and less than 50 bars for the second one.

Several elements and compounds can affect the two processes and their maximum acceptable concentrations are given below:

Tars: Complex organic compounds can be a problem to the procedures and must be reduced to less than 10 ppm.

Halogen species: Concentration of chlorine should be kept below 0.5 ppm.

Nitrogen compounds: The accepted concentration of NH_3 is less than 10ppm for the CH_3OH process and less than 1ppm for the second one. Data about the HCN content is not available.

Heavy metals: Concentrations of As, Hg, Se below 0.5ppm

Alkali species: The presence of alkalis should be reduced to less than 0.5 ppm.

Water content: Water content is a problem above 0.1% for process A and above 50ppm for process B.

All collected data for the requirements of the various processes are presented in Table 1.

Table 1: Requirements on the purity levels of the syngas for all processes

	H ₂ O ₂		Higher Alcohols		MeSH	
	Anthraquinone process	Direct Process	Cu-Based Catalysts	MoS ₂ – based catalysts	CH ₃ OH process	H ₂ /CO process
Temperature (°C)	0-45	40-60	250-350	250-350	< 400°C	< 400°C
Pressure (bar)	3-6	10-300	30-80	30-80	< 25 bars	< 50 bars
Desired components ratio	H ₂ >99.8%	H ₂ >99.8%	H ₂ /CO: 1 (1-2)	H ₂ /CO: 1 (1-2)	H ₂ S:CH ₃ OH <15 H ₂ = S (mol/mol)	H ₂ /CO ≥ 2 H ₂ S/CO ≥ 1 (mol/mol)
Tars	No tars	No tars	<0.1 mgnm ⁻³ [1]	<0.1 mgnm ⁻³ [1]	< 10 ppm	< 10 ppm
Sulfur species (H ₂ S, COS)	<1ppm H ₂ S	<1ppm H ₂ S	H ₂ S: [2,3] 0.1ppmv-60ppb COS: <9ppm[3]	H ₂ S: [4,5] 100ppmv COS: <9ppm[3]	-	-
Halogen species	Cl ₂ : <1ppm NaCl: <60ppm	-	<1ppb [6]	<1ppb [6]	Cl < 0.5ppm	Cl < 0.5 ppm
HCN	Possible catalyst poison: <1ppm	Possible catalyst poison: <1ppm	<10ppb [8]	<10ppb [8]	No data	No data
NH ₃	<10ppm	<10ppm	<10ppm [1,3]	<10ppm [1,3]	< 10 ppm	< 1 ppm
As, Se, Hg	<0.01ppm	<0.01ppm	ppb levels [9]	ppb levels [9]	< 0.5 ppm	< 0.5 ppm
Alkali species	? ppm (NaCl<60ppm)	No data	No data	No data	< 0.5 ppm	< 0.5 ppm
Water content	Below saturation at tP	Below saturation at tP	No data	No data	< 0.1 %	< 50 ppm
CO ₂	Possible carbonistaion of Pd Catalyst	<1ppm	-	-		
CO	<1ppm	<1ppm	-	-		

2.4 Power & Heat Production

Particles: Char particles, ash and bed material are carried with the syngas and cause erosion and mechanical failure to the prime mover components and especially to the fuel gas booster and turbine blades and must be removed to less than 0.1-0.2 g/m³.

Tars: These are a mixture of complex organic compounds, mainly aromatic nature, of large molecular weight which when the product gas is cooled below 400 °C start to condense and

form aerosol mixtures that are very difficult to separate. Tars can cause severe problems to all mechanical equipment after the gasifier and during combustion they cause the formation of soot which attacks the turbine blades.

For these applications there are precise requirements, and as an engine manufacturer presupposes, and are presented below:

Table 2: Requirements applicable for combustion engines

Component	Unit	Limit value
PAHs	$\text{g/ m}^3_{\text{n,dry}}$	0.001 – 0.002
Methanol (CH_3OH)	$\text{g/ m}^3_{\text{n,dry}}$	0.3 – 0.4
Acetic acid (CH_3COOH)	$\text{g/ m}^3_{\text{n,dry}}$	0.5 – 0.6
Tars	$\text{g/ m}^3_{\text{n,dry}}$	1.5 – 2.5
Particles	$\text{g/ m}^3_{\text{n,dry}}$	0.1 – 0.2
Calorific value (dry gas)	$\text{MJ/m}^3_{\text{n,dry}}$	6.0 – 7.5
Calorific value (wet gas)	$\text{MJ/m}^3_{\text{n,wet}}$	5.5 – 6.6
Gas temperature	$^{\circ}\text{C}$	38 – 42

For gas turbines, the same acceptance of pollutants as mentioned for engines can be expected, but the gas temperature should be higher. For turbines it is essential to maintain the temperature of the syngas above the dew point of condensable hydrocarbons (tars).

Alkali metals (Na and K): In the high temperatures of the gasification unit, alkalis, inherent in the biomass ash, volatilise and cause corrosion to mechanical parts of the prime mover. Their concentration must be lowered to less than 0.25mg/m^3 .

Nitrogen Compounds: Nitrogen can produce NH_3 and HCN in the gasification environment. These cause NO_x emissions increase during combustion of the syngas.

Sulfur and Chloride compounds: These are usually H_2S , COS and HCl respectively and cause acidic corrosion to the mechanical parts of the prime mover. The problems are more severe in the cases of biomass, where S and Cl are in significant concentrations in the ash.

3. Discussion on gas cleaning

Based on the available data described above, there are certain gas cleaning requirements in order to achieve the desired purity of the syngas for the various syntheses and power use. The content of sulfur, alkali, nitrogen and halogen species, tars, particles and water content must be controlled.

3.1 Available techniques for gas cleaning

3.1.1 Partial Oxidation (POX) unit from DTI

The aggregate used in connection with POX research includes two reactors with external heat control. The first reactor which is cyclone-shaped is used for Thermal Partial Oxidation (TPOX). Air or oxygen and steam are introduced to the reactor chamber in a way that secures an effective mixing with the syngas. The reactor is designed to withstand a temperature of 1200 °C. The second reactor, used for Catalytic Partial Oxidation (CPOX), is a cylindrical with a fixed bed filling of granulated, active material (dolomite, catalyst etc.). The bed is equipped with gas outlet on different levels, for control and monitoring of gas composition (tar conversion).

Different types of syngas from Danish gasifiers (updraft, downdraft and fluidized bed) are used in the tests, which will include the examination of tar conversion through variation of process condition.

The result of tar removal is difficult to predict since it depends on different parameters such as:

- Type of tar (high or low temperature)
- Tar concentration
- Reactor conditions (temperature, oxygen or air ratio, air/gas mixing, retention time etc.)
- Efficiency of catalytic material
- Degradation, fouling and poisoning of catalyst.

The expectation is that the result for TPOX will be 200-500 mg tar/m³_{n, dry} and for CPOX 100-200 mg tar/m³_{n, dry}.

Limitations

Tars and Particles: A heavy dust load (solid particles) will always be a limitation for the POX process and in particular a sticky mixture of condensable tars and particles. In this case the POX unit's supply tube can clog up. The tube should be as short as possible and in case of updraft gas heating of the supply tube is strongly dissuaded because of increased clogging tendency. Once the sticky particles have reached the TPOX reactor, the problems are overcome. Organic particles and tar will decompose and the cyclone will separate the majority of remaining particles. Nevertheless, inorganic particles are a problem for the CPOX process, since the fixed catalytic bed tends towards clogging up in case of heavy dust load. In this case the preheated cyclone is used as a dust sampling device upstream the CPOX unit. Hereby, the chief part of the dust is removed from the gas, thus, fouling of the downstream

catalyst is reduced. Higher resistance against fouling can also be obtained through the right choice of catalyst design.

A monolithic honeycomb catalyst is much more tolerant towards particulate pollution than a fixed bed with catalytic pellets. Usually test units have higher tolerance against pollutants than commercial plants because of relative short test runs.

Time and load of particles and tars: The limitation of the POX unit is close connected to time. It is not exactly known, how long a test can run before the system must be cleaned or regenerated. Based on the experience of DTI, on updraft gas, 1000 mg particles/ m³_{n, dry} and 50 g tar/m³_{n, dry} do not give any problems within several days of operation. On downdraft gas previous operations with 2000 mg particles/ m³_{n, dry} and 2000 mg tar/ m³_{n, dry} did not appear any problems.

Deactivation of catalyst by sintering: This phenomenon occurs in oxidizing atmosphere and high temperature. Sintering should not form a problem in our case because POX takes place under substoichiometric conditions and the temperature is properly controlled.

Deactivation by coke formation: The formation of coke is suppressed by adding steam.

Deactivation by sulfur poisoning: Most catalysts tolerate a sulfur content of 10 ppm in the feedstock. Usually biomasses do not form any problems on account of sulfur content. Incidentally *Lombard et al.* reported full regeneration of nickel catalysts poisoned by sulfur through treatment with pure steam at 720 °C for 15 h.

3.1.2. Purification by Haldor Topsøe

For decades, Topsøe's complete line of feed purification catalysts has proven very effective for economical removal of unwanted compounds in hydrocarbon feedstocks.

Purification Steps

- Hydrogenation
- Absorption
- Final Purification

Hydrogenation Step

The hydrocarbon feedstock may contain various compounds of sulfur and chlorine as well as olefins, which have to be removed to minimise problems in the downstream units. Feed purification is commonly initiated by a hydrogenation step, where organic compounds are converted with hydrogen into inorganic hydrogen sulphide and hydrogen chloride over a

hydrogenation catalyst. The hydrogenation step is necessary, as organic compounds are not as easily absorbed on downstream absorbents as inorganic compounds. A problem, which may arise when processing various types of feedstocks, is a large variation in sulfur content in the feed. The hydrogenation catalyst, which normally is a cobalt or nickel molybdenum type, possesses the highest activity in the sulphided state. If the feed is essentially sulfur-free for longer periods, the sulfur on the catalyst will gradually be stripped off and the catalyst activity will decrease. When switching to a feed with high sulfur content, the catalyst activity may not be sufficient for converting all the organic sulfur. This problem can be solved by continually adding a small quantity of sulfur to the sulfur-free feed, ensuring that the catalyst is kept in its sulphided state, at all times. If the feedstock contains olefins it may have to be treated in a special way. Hydrogenation of olefins is a strongly exothermic reaction. It is generally recommended to limit the operating temperature to 400°C/750°F in order to prevent possible carbon formation. If the olefin content in the feed is high, the temperature increase across the catalyst may result in a temperature higher than the allowed maximum. In such case, recycle of part of the hydrogenated gas can solve the problem.

Absorption Step

Downstream the hydrogenator all sulfur and chlorine compounds are now present as inorganic hydrogen sulphide and hydrogen chloride. The hydrogen sulphide is absorbed effectively and rapidly on zinc oxide, which today is the most widely used chemical absorbent. If the feedstock contains chlorine, an additional chemical absorbent is installed.

Chlorine Absorption

Chlorine is a serious potential problem and may deactivate downstream catalysts and/or lead to corrosion in downstream equipment. Chlorine compounds are mainly a problem in certain refinery off gases as well as natural gas spiked with landfill gas.

Topsøe has developed a superior chlorine absorbent with high absorption capacity at low as well as high temperatures. The absorbent should be installed upstream the zinc oxide to avoid formation of zinc chloride and normally downstream the hydrogenation catalyst, as only chlorine in form of hydrogen chloride is reacting with the absorbent.

Sulfur Absorption

Zinc oxide reacts with hydrogen sulphide according to the following equation:



Based upon detailed analyses of catalysts downstream the sulfur absorption section, it is Topsøe's experience that a system of hydrogenation followed by zinc oxide absorbers can bring the sulfur concentration down to a level around 0.005 vol ppm. In order to achieve this,

Topsøe has developed a series of zinc oxide absorbents, which provide a very high absorption capacity for all applications.

When a zinc oxide bed has been in operation for some time, the axial distribution of sulfur in the bed will ideally have a sulfur profile as illustrated in the graphic above (Fig. 4).

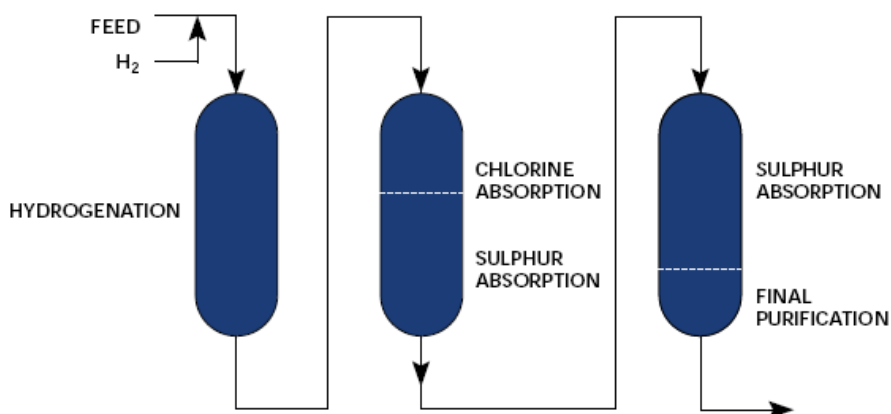


Figure 4: Diagram of the purification process by Haldor Topsøe

Final Purification

Some plants experience problems due to insufficient desulfurisation of the feedstock. Reasons for this may be a large variation in sulfur content in the feed, low operating temperature, high carbon dioxide or water content in the feed. In these cases the solution may be installing a special guard catalyst in the bottom of the zinc oxide reactor for final clean-up of sulfur. For this purpose, Topsøe has developed a catalyst with a very efficient pick-up of all sulfur down to nil. The sulfur pick-up takes place by chemisorption, but at certain conditions, bulk absorption will take place as well.

3.2 Design of gas cleaning system with activated carbon from CERTH

In most cases the scavenging techniques that will be tested, will be based on dry sorbent and specifically, activated carbon for removing trace detrimental for downstream applications. The dry processes minimize water effluents. Furthermore, the currently designed gas cleaning system will make use of the activated carbon that will be produced from WP6.4. A preliminary description of the process is shown on Fig. 5.

Activated carbons will be tested on their removal efficiency on tars, sulfur and halogens species. Requirements on the levels of purity of the syngas have been reported. However, available data does not exist for all possible components found in the syngas. Analyses of the available types of biomass will provide further information on the concentrations of several elements in the initial gasification feedstocks. In the presence of trace elements like Hg, Se

and As in the feedstock materials, activated carbons will also be used for removing them from the syngas.

Furthermore, online measurements of the producer gas from solid biomass gasification will give information on the levels of the concentrations in the syngas. Depending on the results, the actual gas cleaning scheme will be finalized.

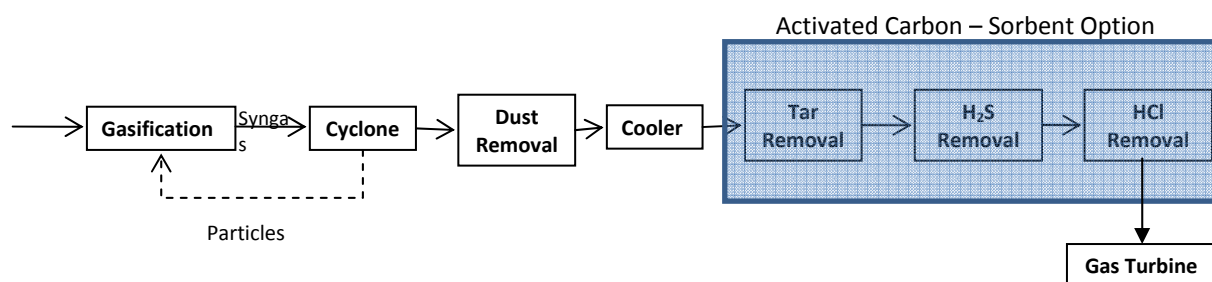


Figure 5: Gas cleaning scheme with the use of activated carbon.

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