

# **A novel approach for removing ammonia and TAR in gasification processes**

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This paper makes a comparison between a traditional ATR and a membrane configuration. Both systems are based on monolith noble metal catalysts.

The ATR membrane reactor has been selected for comparison with the traditional scheme because it does not require the use of combustion air increases tar conversion and allows to operate at a slightly lower temperature. Optimal values of the operating variables parameters have been also been determined. Results show that with the proposed membrane scheme it is possible to obtain higher CH<sub>4</sub> and NH<sub>3</sub> conversions and an almost total TAR conversion.

These results are very encouraging but have to be confirmed by experimental data.

## **1. Introduction**

Gasification of carbonaceous materials represents an interesting alternative for exploiting renewable materials to produce a rich hydrogen gas.

The proper use of such syngas requires the removal of contaminants such as NH<sub>3</sub> and TAR, whose content results from raw material type and gasification conditions.

Within the gasifier, the biomass is gasified at 700÷1000 °C and converted to a mixture of hydrogen, carbon monoxide, carbon dioxide, nitrogen (if air is used), methane and small amount of light hydrocarbons. The concentration of impurities ranges from 5 to 30 g/Nm<sup>3</sup> for particles and 0.5 to 30 g/Nm<sup>3</sup> for alkali metals. The tar content in biomass gasification gas varies from 5 to 75 g/Nm<sup>3</sup>, depending on the type of gasifier and the characteristics of the feedstock. The tar is always present in gasification gas as a side product and can easily plug the downstream process equipment (Zhang, Y. et al., 2002). Object of this study is the tar removal by autothermal reforming of the raw gas from a pressurized gasification. This study carries out a comparison between two different tar cracking plant configurations and it analyzes the influence of the main process parameters on tar and ammonia conversion. The simulations have been carried out at different reforming temperature in the range from 840÷900 °C to minimize coke formation over the catalyst bed. The composition assumed is a typical raw gas from a fluidized bed gasifier using air at a temperature of 900÷950°C.

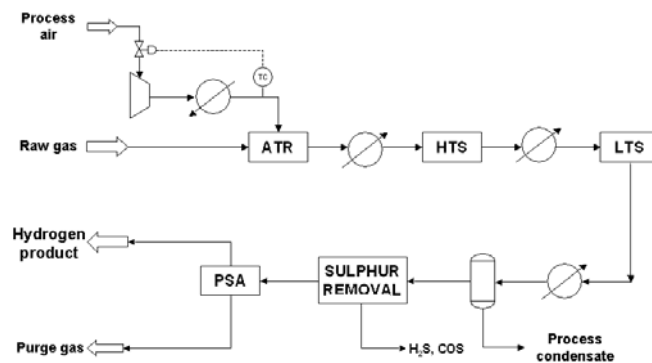
Raw gas composition			
Component	% vol	Component	% vol
H <sub>2</sub>	12.42	O <sub>2</sub>	0.00
CH <sub>4</sub>	2.61	Ar	0.00
C <sub>2</sub> H <sub>6</sub>	0.02	H <sub>2</sub> O	14.49
C <sub>2</sub> H <sub>4</sub>	0.87	NH <sub>3</sub>	0.33
CO	14.94	H <sub>2</sub> S	0.03
CO <sub>2</sub>	12.09	HCl	0.07
N <sub>2</sub>	41.64	C <sub>10</sub> H <sub>8</sub>	0.49

**Tab. 1 –Typical raw gas from a fluidized bed air gasifier: mass balance data for TPS Termiska plant gasifying organic fuels (Biffaward Programme on Sustainable Resource Use Report: Thermal methods of municipal waste treatment, 2004).**

## 2. System configurations and components

The first scheme, scheme A, depicted in Fig.1, is composed by the following main unit operations:

- ATR REFORMING  
The raw gas outlet from the pressurized gasifier is fed to the ATR reforming at 900°C. The heat of reaction is supplied directly by adding process air that regulates the ATR outlet temperature.
- SHIFT REACTION  
The syngas is converted in two shift stages, HTS and LTS.
- PSA  
The LTS outlet is cooled and sent to the PSA unit where hydrogen and purge gas are obtained. The purge gas could be recycled back to the gasifier. Before PSA unit H<sub>2</sub>S removal is foreseen.



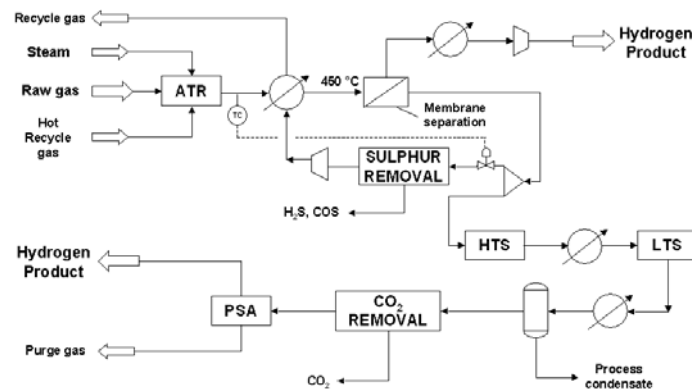
**Fig. 1 – Scheme A: ATR REFORMING - Overall System Configuration**

The second configuration, scheme B, differs from the previous one for the following points:

- Introduction of a membrane separation unit downstream of the ATR. Presence of a recycle stream constituted by the retentate of the membrane that is

- compressed and recycled back to the gasifier before being sent to the ATR reactor. The recycle stream is used to control the reforming temperature.
- Presence of two clean-up stages. The first one removes steam,  $H_2S$  and  $COS$  from the recycle stream before the compression step and second one removes the  $CO_2$  from the remain retentate before going to PSA unit.

The proposed scheme is depicted in the Fig.2.



**Fig. 2 – Scheme B: ATR MEMBRANE REFORMING - Overall System Configuration**

### 3. Process schemes description

In the proposed scheme A, first the raw gas from the pressurized gasifier is mixed with air and it is sent to a catalytic autothermal reforming for tar conversion. Then, the syngas is cooled down at  $320^{\circ}C$  before entering a first shift reaction step (HTS) and it is further cooled down at  $220^{\circ}C$  before the second shift reaction step (LTS).

Finally steam is removed as process condensate by cooling down the syngas before entering to the PSA where hydrogen is recovered.

In the proposed scheme B, the raw gas is first mixed with steam before entering in the autothermal reactor. The reactor outlet temperature is controlled by the recycle stream from the membrane separator. Syngas is cooled down at  $450^{\circ}C$  and sent to the membrane separation unit where hydrogen is recovered. A part of the retentate stream exiting the membrane separator is recycled back to the process after  $H_2S$  and  $COS$  removal, while the remaining part is sent to the PSA unit after shift conversion steps and  $CO_2$  removal. PSA unit allows to obtain additional hydrogen.

The most important step in the raw gas purification is the TAR catalytic conversion. The total TAR fraction of the raw gas contains aliphatic and aromatic compounds; the gasifier typology and the gasifying agent determine its content, but only in high temperature gasifier ( $>1200^{\circ}C$ ) its presence may be neglected (G.Iaquaniello, A. Mangiapane, 2005). The reactor is equipped with a new monolith noble metals catalyst, provided by Engelhard (now BASF), which was successfully tested for diesel application (G.Iaquaniello, A. Mangiapane, 2005). At significant lower catalyst

temperature an undesirable coke formation occurs which is mainly due to hydrocarbon cracking, therefore any temperature lower than 830°C should be avoided. The amount of coke deposition also depends on the monolith temperature: at lower temperature the tendency of coking is rising; it also rises locally if there are temperature mal-distributions due to non-accurate re-heating. Coke deposits can be removed by chemical reaction with steam (and/or) air/oxygen.

#### 4. Results and discussion.

The simulations of both schemes are carried out assuming a 10,000 Nm<sup>3</sup>/h hydrogen production as reference. Both configurations have been optimized respectively acting on air temperature preheating and steam to carbon ratio.

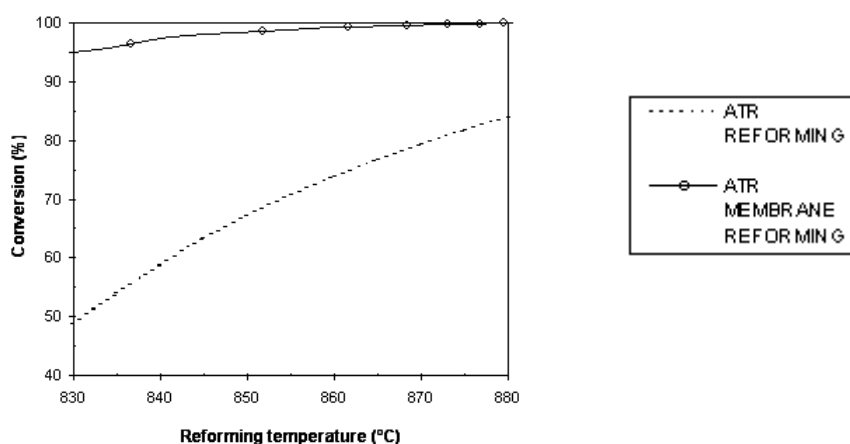
For scheme A the influence of air temperature preheating on air flowrate is limited (around 10%), for the comparison we assumed an air preheating of 350°C.

For scheme B the influence of steam to carbon ratio is more evident for low recycle ratios and milder for high recycle ratios. For the comparison we assumed a steam to carbon ratio of 2.5 because it is possible to obtain very high conversions of CH<sub>4</sub> and NH<sub>3</sub> for all the range of reactor temperature considered (Fig.3).

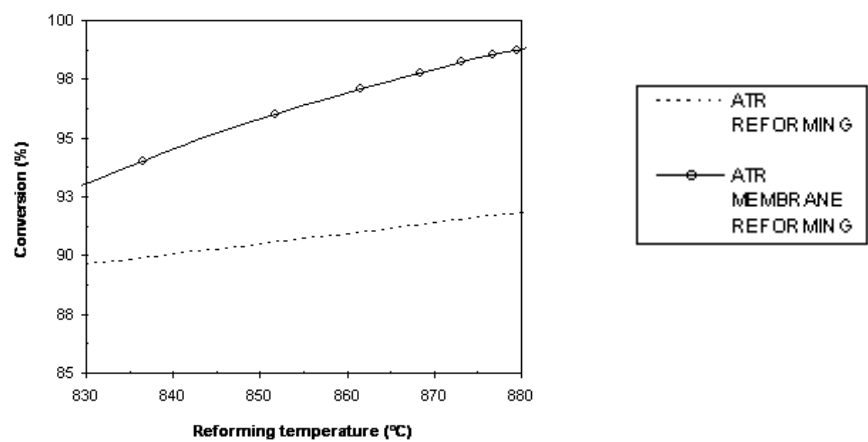
TAR conversion cannot be simply analyzed through the simulation due to the fact that C<sub>10</sub>H<sub>8</sub> used for TAR simulation is completely converted to CH<sub>4</sub>. So tar conversion is evaluated indirectly relating it to the methane content after the reforming.

The results show that for the same reforming temperature with scheme B it is possible to obtain higher CH<sub>4</sub> and NH<sub>3</sub> conversions, comparable overall power absorbed and a feed rate reduction of about 35% at the same H<sub>2</sub> production rate.

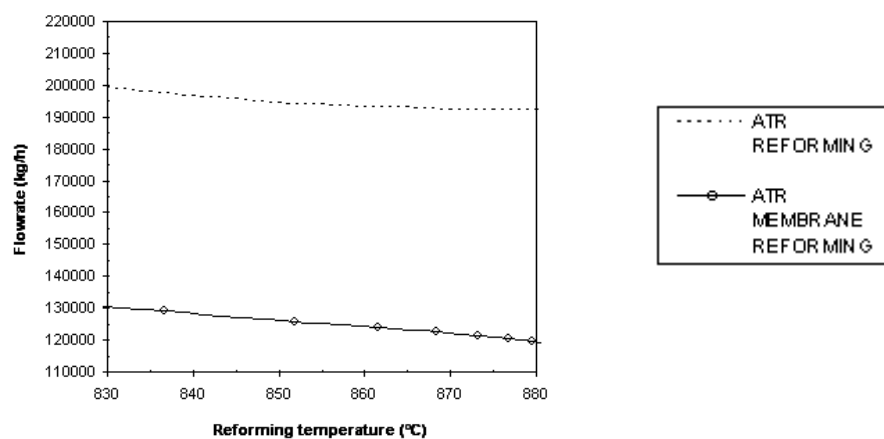
Furthermore such a CH<sub>4</sub> conversion makes possible to draw the conclusion that tar conversion can easily outrun the 90-95% of the conventional schemes and approach 100% conversion.



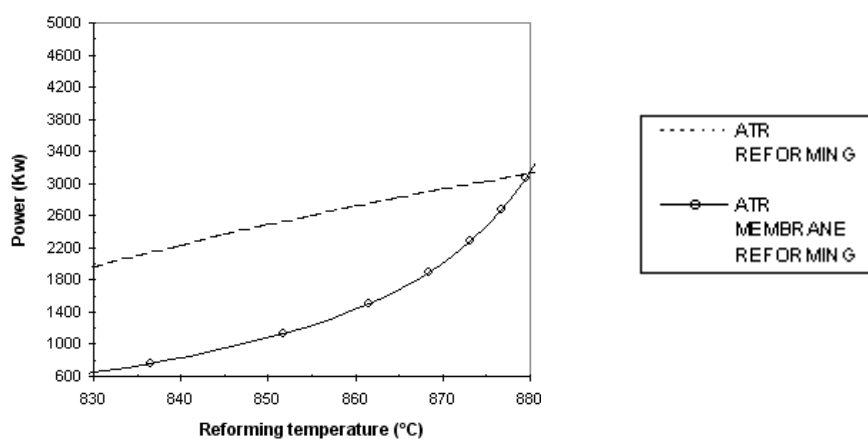
**Fig. 3 – CH<sub>4</sub> conversion versus the reforming temperature**



**Fig. 4— NH3 conversion versus the reforming temperature**



**Fig. 5— Feed Flowrate versus the reforming temperature**



**Fig. 6 – Power required for compression versus the reforming temperature**

## 5. Conclusions.

TAR removal was studied in a traditional ATR (scheme A) and in a membrane reactor (scheme B).

For the membrane reactor (scheme B) a split architecture was selected: an ATR reactor based on monolith noble metal catalyst followed by a ceramic membrane separator.

Such theoretical analysis confirmed the advantages of the membrane reactor architecture in comparison with a traditional ATR reactor.

Our results show that not only  $\text{CH}_4$ , TAR and  $\text{NH}_3$  conversions are higher but the fact that heat for the reactions is extracted from the gasifier and not from the  $\text{H}_2$  content of syngas allows to produce about 35% more hydrogen.

Power absorbed for both configurations are similar. Optimal values of the operating variables parameters have been also been determined.

These results are very encouraging but have to be confirmed by experimental data.

Technical feasibility must be verified in order to integrate the recycle stream into the gasification unit, which would allow to transfer heat from the gasifier to the ATR reactor.

## 6. References

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