Production of Hydrogen from Bio-ethanol

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ABSTRACT:

IFP and HyRadix are collaborating in the development of a new hydrogen production system from liquid feedstock such as bio-ethanol. Reducing greenhouse gas (GHG) emissions along with high hydrogen yield are the key objectives. Market application of the system will be hydrogen refueling stations as well as medium scale hydrogen consumers including the electronics, metals processing, and oils hydrogenation industries.

The conversion of bio-ethanol to hydrogen will be performed within a co-developed process including an autothermal reformer working under pressure. The technology will produce high-purity hydrogen with ultra-low CO content. The catalytic autothermal reforming technology combines the exothermic and endothermic reaction and leads to a highly efficient heat integration. The development strategy to reach a high hydrogen yield target with the bio-ethanol hydrogen generator is presented.

KEYWORDS : *hydrogen, generator, reformer, autothermal, ethanol*

Introduction

IFP is an independent industrial research and development, education and training, and information center active in the fields of oil, natural gas, and the automobile. Its activities cover all aspects of oil and gas processing. IFP is also very active in the field of pollutant emission reduction.

HyRadix provides proven, on-site hydrogen generation systems and supply solutions. HyRadix serves the global market by providing dependable hydrogen solutions for industrial and consumer manufacturing processes and transportation refueling applications and is meeting the growing global demand for lower-cost hydrogen.

IFP and HyRadix are collaborating for the development of a new hydrogen production system from liquid feedstock such as bio-ethanol. Both companies believe that environmental aspects and hydrogen production efficiency are the key objectives for the success of the product. Market application of the system will be hydrogen refueling stations as well as medium scale hydrogen consumers including the electronics, metals processing, and oils hydrogenation industries.

The conversion of bio-ethanol to hydrogen will be performed within a co-developed process including an autothermal reformer working under pressure. The technology will produce high purity hydrogen with ultra-low CO content. The catalytic autothermal reforming technology combines the exothermic and endothermic reaction and leads to a highly efficient integration and utilization of available heat.

HyRadix presently offers hydrogen generators under the product name of Aptus™. The current Aptus products are available in various sizes and operate on either natural gas or LPG blends. The collaborative work will focus on the development of an Aptus system which can operate on various liquid feedstocks, with the first being bio-ethanol. This new hydrogen generator is called Ethanol Aptus in this article. The development of the Ethanol Aptus is based on the existing Aptus product for natural gas, which will be referenced as Natural Gas Aptus in this article.

This article will begin by reviewing the types of ethanol currently produced worldwide, the current commercial applications of ethanol and the factors contributing to the growing interest in producing hydrogen from bio-fuels. It then will describe the R&D approach IFP and HyRadix are taking in developing the Ethanol Aptus.

How Ethanol is Produced

Presently, the two main types of bio-fuels are ethanol, used in gasoline engines, and vegetable oil methyl esters (VOME), with applications in diesel engines. Of the two, ethanol is the most prevalent. Brazil and the United States accounted for most of the 2004 global ethanol production of approximately 25 Mt, which has increased at an average growth rate of 15% for the past 5 years. By comparison, about 2 Mt of VOME were produced worldwide in 2004, primarily in Europe, with production increasing at an average growth rate of 30% over past 5 years.

Bio-ethanol is made from two types of crops: sugar-producing crops (sugar cane, sugar beets) and amylaceous plants (wheat, corn). The production process for each requires a fermentation stage to convert the sugar to ethanol, as well as an advanced distillation stage to separate the alcohol from water. Large volumes of co-products also are produced. Figure 1 gives an overview of the ethanol production process.

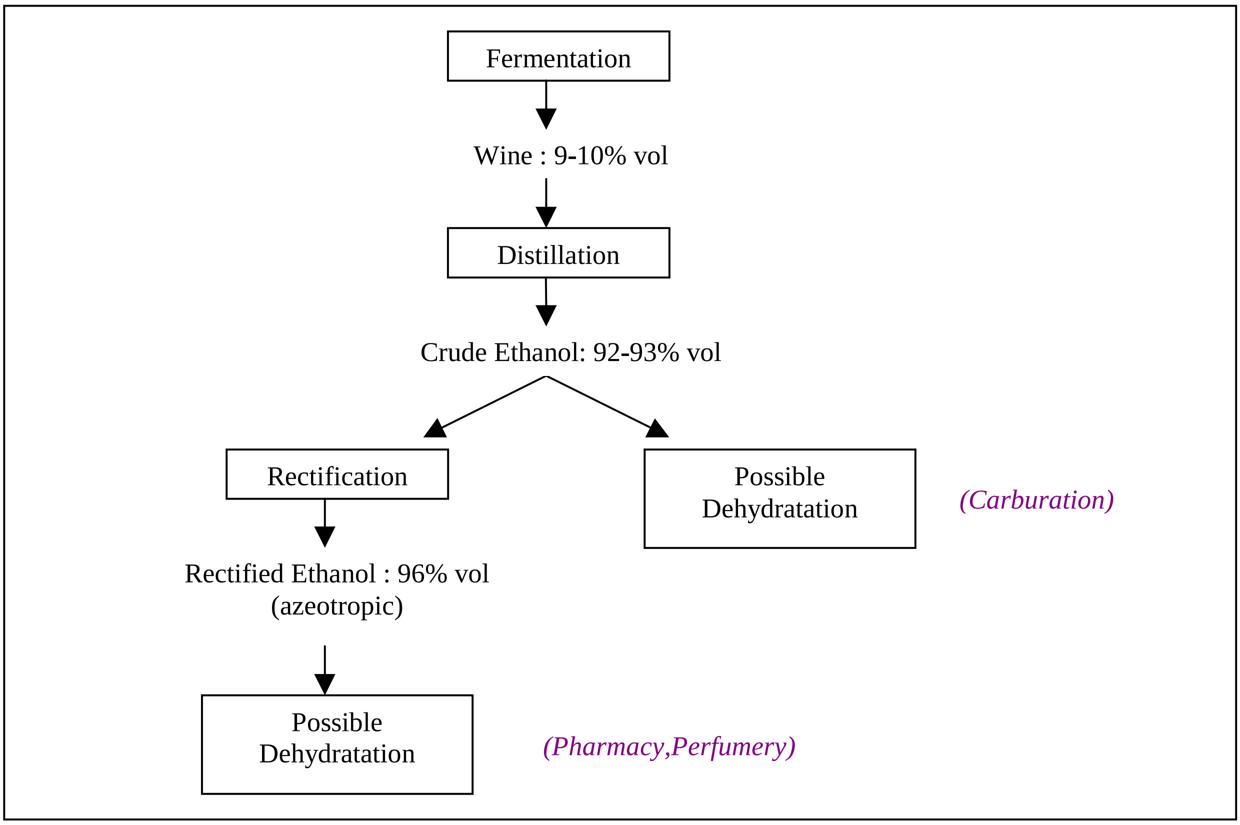

Figure 1: *Main steps of ethanol production process*

There are four primary types of ethanol:

- Non-dehydrated crude ethanol, 93% by volume, contains water and impurities
- Dehydrated crude ethanol, 99.7% by volume
- Non-dehydrated rectified ethanol, 95% by volume (azeotropic with water), with impurities such as aldehydes and ketones removed through successive distillations
- Dehydrated rectified ethanol.

Commercial Applications of Ethanol

The main ethanol market is the transportation sector, which currently consumes more than 75% of ethanol production. Ethanol can be used pure, in a blend or in its ether form (ETBE), which is obtained from a reaction with refinery isobutene. If it used pure or in a very high concentration (e.g. 85% or E85), a variety of engine modifications are necessary. No such modifications are required with lower ethanol blends of 5% to 10%. Currently, General Motors, Ford, DaimlerChrysler, PSA and Renault) have commercialized vehicles which run on both E85 and gasoline.

IFP and HyRadix believe that transportation will continue to be the primary ethanol application for the foreseeable future and thus have chosen to use the ethanol standards associated with the transport sector for the Ethanol Aptus.

Why produce Hydrogen from Ethanol?

The advantages of bio-fuels are well known: they provide an alternative to liquid fossil fuels and reduce greenhouse gas (GHG) emissions. Recently, much international attention has been focused on GHG emissions because of their role in global warming. These discussions have fueled interest in broader application of bio-fuels.

It is difficult to quantify the reduction in GHG emissions achieved through use of bio-fuels because performance is affected by many factors, such as the types of crops used, the weather conditions and agricultural practices under which they were grown and the method used to transform the bio-mass into fuel. These factors can produce significant variance in GHG emissions. Bio-ethanol produced from sugar cane, for example, can cut GHG emissions by as much as 90% compared to a petroleum equivalent pathway, whereas ethanol produced from wheat grown in the northern hemisphere yields only a 15% reduction in GHG emissions.

Efforts must be made to enhance the environmental performance of bio-fuels, and several options are possible. One is reducing the fossil fuel consumption of the ethanol production units. Another is producing ethanol from lignocellulosic materials such as wood or straw. These materials require less fertilizer than the current crops, which reduces the release of N_2O to the atmosphere - a more harmful GHG than CO_2. In addition, the lignin that cannot be converted into ethanol may be use for combined heat and power (CHP) instead of fossil energy in the industrial ethanol production unit. These new pathways to ethanol production can reduce GHG emissions by as much as 90% while dramatically reducing fossil energy consumption on a life cycle analysis compared to the equivalent fossil energy route.

After more than 20 years of industrial development, the outlook for bio-fuels now looks bright. Public authorities are renewing support for bio-fuels and have set ambitious consumption goals that will more than double the world’s bio-fuel production by 2012. Furthermore, very ambitious targets have been set for use in the transportation sector calculated on energy basis: 5.75% by 2010, and 8% by 2020 in Europe; 4% by 2010 and 20% by 2030 in the United States. Recent developments indicate that the use of bio-fuels, previously confined to a handful of countries including Brazil and the United States, is “going global” and a world market may emerge. However, these prospects could eventually be limited by constraints relative to resources and costs. The future of bio-fuels probably depends on the development of new technologies to valorize lignocellulosic substances such as wood and straw.

Approach to develop Ethanol Aptus

In developing the ethanol based generator, IFP and HyRadix decided to build on HyRadix’s commercially proven Aptus hydrogen generation system, which employs catalytic autothermal reforming technology and uses natural gas or LPG as the feed stock. Like the Natural Gas Aptus, the Ethanol Aptus will be developed through a process of optimization studies, development and testing of critical devices, catalyst testing and prototype construction and operation to validate the performance and economics of the product.

The hydrogen generator has five main sections. First is the feed section, where contaminants are removed from the feedstock and pressure and flow rate are regulated. Next is the reaction section, the heart of the process, where the feedstock is converted to syngas in a catalytic auto-thermal reactor. The heat recovery section, incorporating exchangers, boilers and superheaters, overlaps the other sections and ensures optimal heat recovery between effluents and feeds, to maximize yields. In the hydrogen purification section, the syngas is converted to high purity hydrogen at high pressure using pressure swing adsorption (PSA) technology. Finally, the burner section ensures the combustion of the PSA waste gas to provide energy to the system and also supplies the heat energy for start-up of the plant by combusting the feedstock.

Figure 2 below highlights the major points on which IFP and HyRadix are working to redesign the Natural Gas Aptus to the Ethanol Aptus.

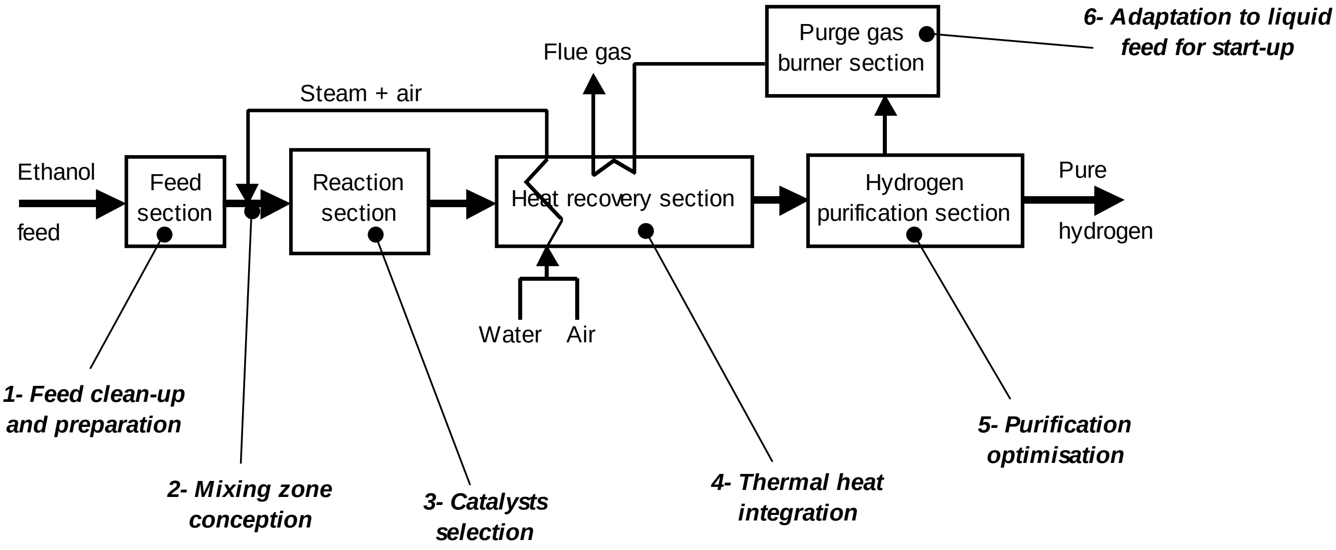

Figure 2: *Overall scheme of Ethanol Aptus with major axis of development*

Process studies

Like the Natural Gas Aptus, the Ethanol Aptus is not just a reformer reactor but rather a full system integrating feed preparation, thermal heat integration, hydrogen purification and effluents management. The development of the complete system begins with process studies.

Process studies involve the investigation of different equipment arrangements and various operating parameters in order to develop an economical product. This is an iterative methodology that needs to take into account multiple factors including efficiency, environmental performance, operating flexibility, materials selection, safety constraints, capital requirements and operating costs.

When evaluating a new hydrogen production system, the most important criterion is the overall cost of produced hydrogen, taking into account investment, feedstock and offsite costs. Unfortunately, not all of these parameters are known at the outset of the study. Therefore, it is necessary to choose representative technical criteria to compare and select options. For a hydrogen production unit from fuel, it is quite obvious to select the net hydrogen efficiency that is defined below:

Net hydrogen efficiency: ratio $$\frac{(H_2\ flowrate\ \ in\ pure\ hydrogen\ stream)\times(H_2\ LHV)}{(Unit\ \ feed\ \ flowrate)\times(Feed\ LHV)}$$

The net hydrogen efficiency depends on the system's thermal integration, which is determined by the flow scheme, exchanger sizing, reformer operating conditions, catalyst activity, and the purification section's performance. Unfortunately, in most cases an improvement in efficiency typically results in higher costs in other areas. Thus, process scheme development requires a compromise between high hydrogen efficiency and investment cost.

Two examples will illustrate this principle. First, the hydrogen generation system uses the available energy from reformer effluent and purge gas (once burned) to preheat the reactants and more particularly to produce process steam. HyRadix and IFP's approach is to maximize the steam to carbon ratio as long as energy can be recovered from effluents. Higher steam to carbon ratios gives higher net hydrogen efficiencies, but at the same time it requires larger size heat exchangers. Therefore, an equilibrium has to be found between the energy recovery and the cost of exchangers.

Second, carbon monoxide in the autothermal reformate could be converted to hydrogen through a water gas shift reactor to further increase the hydrogen production and subsequently increase the net hydrogen efficiency. However, this step requires additional investments for the reactor itself and the associated temperature control loop. Again, an economic study is needed to help determine the correct decision.

IFP and HyRadix process simulations show that the Aptus unit designed to process ethanol can achieve hydrogen plant efficiency of 64% to 66%., in part by using heat available within the process to vaporize the liquid feed. Other options are being reviewed which can increase the efficiency beyond this range.

Environmental performance is linked to the feedstock source and the feed clean-up strategy. IFP and HyRadix are investigating several options for contaminant removal. Available options depend on where the contaminants are removed in the process scheme. If sulfur is removed upstream in the autothermal reforming process, the sulfur components are typically alkyl thiophene and mercaptans when gasoline is used as the denaturant. If sulfur is removed downstream of the autothermal reforming process, the sulfur component is mainly hydrogen sulfide. This second option requires the autothermal reforming catalyst to operate in the presence of sulfur. The chloride contained in gasoline denatured ethanol will also need to be removed since it poisons the catalysts and may also cause corrosion issues in downstream equipment.

Overall unit flexibility is not a direct criterion of optimization but it does guide the choice of options and the design of equipment. For example, the PSA waste gas burner must maintain combustion even when the flow rate is low. Another example is the mixing zone upstream of the autothermal reforming catalyst, where at turndown the residence time of the reactant increases proportionally, thus requiring a design which does not exceed the auto-ignition delay. This illustrates that the choice of the turndown ratio can have a major impact on the equipment design.

Material selection also is a key consideration, since it determines the maximum temperature at which equipment can operate. Thus material selection imposes limits for the choice of operating conditions and may indirectly impact the net hydrogen efficiency.

Finally, safety considerations must also guide the scheme optimization. For example, IFP and HyRadix minimize hazardous operation of heat exchangers by dedicating some exchangers to flammable streams and other exchangers to non-flammable streams

Technology development and test of critical devices

As shown on Figure 2, several key points in the process scheme require optimization.

As explained above, the Ethanol Aptus is developed from HyRadix's Natural Gas Aptus platform, a commercially available product. Although some parts of the technology can be adapted directly from the Natural Gas Aptus platform,,several areas must be addressed. As with the natural gas design, the fuel must be fully mixed with the air and steam prior to reforming. With a liquid feed, however, this may require vaporizing the fuel prior to mixing; which would necessitate a proper vaporizer and heat exchanger design. Ethanol has a much lower auto-ignition temperature than natural gas; therefore, the mixing and distribution zone prior to the reforming catalyst must be redesigned relative to natural gas. The technology development for those areas is detailed below.

When processing an impure hydrocarbon, the vaporization phenomenon is spread over a range of temperature. That behavior of the mixture requires some basic precautions: the feed vaporizer must prevent distillation that would lead to unsteady flow compositions feeding the reforming catalyst and a suitable temperature cross between hot side and cold side of the heat exchanger must be applied.

To understand the characteristics of the auto-ignition for the ethanol reactants, we investigated the auto-ignition delay of the reactant mixtures at different conditions. When a fuel is mixed with oxygen it is subject to oxidation. The kinetics of the fuel oxidation depends on the exact composition and on the temperature. The speed of oxidation increases exponentially with the temperature. The auto-ignition delay is defined as residence time during which the mixture temperature increases by more than 1°C due to the oxidation reaction. The auto-ignition reflects the relation between the temperature and the time.

Attention must be paid to the design of the zone before the reforming catalyst to avoid auto-ignition. Auto-ignition is detrimental to the net hydrogen efficiency. Figure 3 illustrates the impact of the feedstock on the auto-ignition delay. In order to avoid the auto-ignition, IFP and HyRadix have developed a special design for the autothermal reforming reactor that ensures a high mixing efficiency and distribution of the gas flow over the monolith cross-section in a delay that is lower than the auto-ignition delay of the mixture at the inlet temperature. The mixing and distribution performances of the optimal geometry are determined by CFD calculations. Kinetics software was used to evaluate the auto-ignition delay versus the temperature for the different inlet composition investigated during the process optimization.

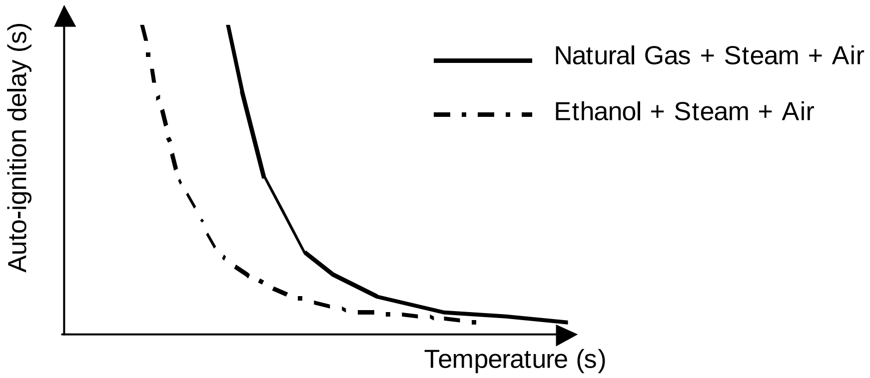

Figure 3: *Auto-ignition delay versus temperature*

Warming the unit from cold is a strategic point as it defines the delay of start-up and therefore the capacity of the system to start-up easily, quickly and at a low cost. HyRadix and IFP investigated several options and compared them on a multi-criteria matrix. The main criteria are the energy source availability, the simplicity and robustness of the device, the investment cost and cost per start-up.

Catalyst testing

The autothermal reformer catalyst is a key component in the ethanol hydrogen generation system. The catalyst to be used in our system will exhibit high activity and hydrogen selectivity, excellent stability over a long operating cycle, and low cost. High resistance to sulfur and other contaminants may also be required. There is very limited information on the development of catalysts for ethanol autothermal reforming, and currently there are no commercially available catalysts specifically developed for an ethanol fueled autothermal reforming process. We selected a catalyst based on our experience with autothermal reforming catalysts for natural gas and LPG and characterized its capability for ethanol autothermal reforming.

We investigated the effects of operating conditions on the hydrogen yield first to determine the optimal conditions for maximum hydrogen efficiency using a micro-reactor. Some of the main parameters for operating conditions are: the mixing temperature, the inlet temperature, the reaction temperature, the gaseous hourly space velocity (GHSV), the steam to carbon ratio (S/C), and the oxygen to carbon ratio (O_2/C). The inlet temperature will depend on the mixing method and the auto-ignition temperature of the reactant mixture. The inlet temperature will also affect the autothermal reforming temperature and the outlet temperature. As for the S/C ratio, it is driven by the global thermal integration and optimization of the process scheme. The O_2/C ratio is directly linked to the targeted outlet temperature for an adiabatic reactor. Generally, higher hydrogen efficiencies are achieved at elevated S/C and/or low O_2/C ratios but as discussed previously these variables are just part of the overall system design and the cost analysis. The optimal GHSV is determined experimentally. Practically, the feed flowrate is increased progressively up to a value where it is observed that the composition obtained no longer matched the theoretical thermodynamic equilibrium composition. In this way it is possible to calculate the minimum volume of the catalyst needed for the industrial scale.

Our test results show that the autothermal reforming catalyst we have chosen has high activity with ethanol. Our initial tests with 190 proof ethanol (95vol% ethanol, sulfur free) have shown that the reformate gas composition matched the thermodynamic equilibrium composition even at high GHSV values. We are continuing our work on the catalyst test to determine the optimal operating conditions and to assess its stability and ultimate life. The catalyst will also be tested with denatured ethanol and other commercial grade ethanol fuels to ensure no loss in activity and stability. The strategies for contaminants removal from commercial fuel grade ethanol is still under investigation.

Prototype construction and validation

To complete the development program, a prototype will be built. The prototype will be operated in IFP-Lyon with a hydrogen production capacity of 50 Nm^3/h. The main objectives of the prototype implementation are to:

- Validate the plant start up procedure;
- Validate the heat recovery process and make adjustments if necessary;
- Tune the control loop for push button start-up, normal operation, turn-down operation and shut-down;
- Determine the plant performance with the real pressure drop and heat losses; and
- Enable a precise cost performance evaluation of the Ethanol Aptus.

IFP and HyRadix's objective is to have the prototype built and ready for operation at the beginning of 2007.

Conclusions

In order to develop an environmentally friendly hydrogen generator, ethanol is the first feed selected for the design of a new hydrogen generator. IFP and HyRadix have made the challenging choice of using industrial quality denatured ethanol. It is strongly felt that the only product that will be commercially viable is one that utilizes the ethanol infrastructure currently in place throughout the world. Developing a product that also requires the development of a fuel infrastructure support system will at best delay its acceptance and potentially make it unfeasible.

The process studies already conducted show that high hydrogen plant efficiency is achievable using typical ethanol feed. Using the already proven HyRadix Natural Gas Aptus platform along with IFP's proven experience with liquid feedstock, both companies are confident that an economically viable product that operates on ethanol will be developed from this program. IFP and HyRadix look forward to the operation of a full scale prototype in the beginning of 2007.

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