

Optimal use of Hybrid feedstock, Switchgrass and Shale gas, for the Simultaneous Production of Hydrogen and Liquid Fuels

Mariano Martín^a, Ignacio E. Grossmann^{b,1}

Departamento de Ingeniería Química. Universidad de Salamanca. 37008 , Salamanca (Spain)

Department of Chemical Engineering. Carnegie Mellon University Pittsburgh, PA, 15213

Abstract.

In this paper, we present the optimal simultaneous integration of the production of liquid fuels and hydrogen from switchgrass and shale gas. The process is based on FT technology in which the shale gas is reformed with steam while the switchgrass is gasified, reformed (with steam or partial oxidation). The raw gas is cleaned up, including removal of the sour gases, and its composition is adjusted (using either WGS or PSA) and the liquid fuels are obtained in an FT reactor. The heavy liquids are upgraded using hydrocracking to increase the yield towards FT-diesel. We identify the optimal distribution of products, hydrogen and liquid fuels, as function of the shale gas and switchgrass prices. Production costs for the biomass-shale gas facility are below \$1/gal as long as biomass price is below \$100/t and the price of the shale gas does not go above \$11.5 /MMBTU. Furthermore, hydrogen is produced as long as the demand for liquid fuels is met and there is enough shale gas available.

Keywords: Energy, Biofuels, Alternative fuels, Diesel, Fisher – Tropch

¹ Corresponding author. Tel.: +1-412-268-3642; Fax: +1-412-268-7139.
Email address: grossmann@cmu.edu (I.E. Grossmann)

1.-Introduccion

Over the last decades there has been an effort to develop alternative fuels for transportation. Bioethanol and biodiesel are the most promising due to their compatibility with the current supply chain and automobiles. However, there are a number of challenges to overcome, mainly due to the large demand of fuels and the limited production capacity of biofuels as a result of the need for large harvesting areas, or to switch from first to second generation biofuels to avoid competition with the food chain. Thus, in the meantime hybrid first and second generation biofuels, using corn grain and stover for the production of bioethanol [1] or biomass – fossil fuel feedstock [2-4] can be used to reduce the dependency on fossil fuels and to serve as a bridge between the technologies.

Recently a new source of fossil fuels has been found, shale gas. Shale gas is natural gas that is trapped within shale formations, fine-grained sedimentary rocks. The discovery of the shale gas in the US has greatly decreased the price of natural gas and its volatility, with values as low as \$2/MMBTU (January 2002 and again from February 2012 onwards) in contrast to the high values of \$16/MMBTU in January 2006 [5]. In 2009, 87% of the gas consumed in the US was produced domestically. Thus, the supply of natural gas is not as dependent on foreign producers as is the supply of crude oil, and therefore the delivery system is less vulnerable to interruptions. The availability of large quantities of shale gas will further allow the United States to consume a predominantly domestic supply of gas. According to the EIA Annual Energy Outlook 2011, the United States possesses 2,552 trillion cubic feet (Tcf) of potential natural gas resources. Natural gas from shale resources, considered uneconomical just a few years ago, accounts for 827 Tcf of this resource estimate, more than double the estimate published last year [6,7].

Bioethanol production from switchgrass via thermochemical routes is becoming promising as a substitute for gasoline in terms of production cost [8], in spite of the higher investment required compared to the biochemical route [9]. Biodiesel from algae is also the focus of development by academia, government and industry, ExxonMobil announced a \$600 million program [10-12]. However, the use of Fischer Tropsch technologies from biomass alone have received less attention due to the lower yield from lignocellulosic biomass, higher production cost compared to the production of ethanol from the same raw material or the higher investment cost compared to biodiesel [4, 8, 10, 13-16]. However, the FT technology allows the simultaneous production of FT diesel and

green gasoline yielding a flexible plant. In order to improve the economics, we can help bridge the gap between current fuels and biofuels by using Fischer Tropsch technology with a hybrid source of syngas, shale gas and switchgrass. This would increase the yield to synthetic fuels thereby reducing the dependency on crude oil, while evaluating the production of hydrogen as byproduct, taking also into account the fact that we need a certain amount of hydrogen for the upgrade of FT-liquids.

In this paper, we propose a superstructure optimization and sensitivity analysis for the conceptual design of multiproduct facilities involving the production of green diesel from lignocellulosic switchgrass and shale gas using the FT technology. We consider switchgrass since it is the raw material of choice by the DOE due to the harvesting possibilities in the US and its high yield to biofuels. Furthermore, shale gas is currently widely available in the US so the use of both raw materials to produce liquid fuels may help reduce US dependency on foreign liquid fuels. We first construct a flowsheet embedding the various process units involved in syngas production from the two sources, as well as the synthesis of liquid fuels based on FT technology considering various alternatives for some of the processes. The goal is to optimize the superstructure, the product distribution, and the operating conditions to maximize FT-diesel production, while minimizing the energy input as function of the availability and price of raw materials (biomass and shale gas devoted to this task), and byproduct price (hydrogen) to evaluate the possibilities of such production facilities in a flexible market arena. The optimization of the system is formulated as a mixed-integer nonlinear programming (MINLP) problem where the model involves a set of constraints representing mass and energy balances for all the units in the system as well as design correlations. Next, we perform heat integration of the resulting process developing the heat exchanger network followed by a detailed economic evaluation to determine the production cost of liquid fuels as function of the raw material and byproduct prices and its availability.

2. Overall Process Description

The process consists of five different parts. First, the shale gas is reformed with steam to produce raw syngas. Part of the gas is needed to heat up the furnace since steam reforming is endothermic. On the other hand the switchgrass is gasified. Based on previous work [8], we select indirect gasification followed by reforming (either with steam or partially oxidized [17]) to remove the hydrocarbons generated. The solids are removed together with NH_3 in a wet scrubber and the gas is compressed. At this point, both sources of raw syngas are

mixed. The traces of hydrocarbons are removed in a PSA system with a bed of Silica gel. Next, the composition may need to be adjusted to a molar ratio of $H_2:CO$ from 1 to 2 according to the results by Wang et al [18]. Three alternatives are considered: water gas shift reactor, bypass and hybrid membrane / PSA for H_2 (with a bed of oxides). The split fraction depends on the performance of the gasifier, the shale gas and the tar reformer, which may make this composition adjustment redundant. In case of an excess of hydrogen, it exits the system through the hybrid membrane / PSA.

The third part corresponds to the removal of sour gases, CO_2 and H_2S . According to the study by Martin & Grossmann [8] two technologies operating in sequence are considered for this task: the absorption of the sour gases in monoethanol amine (MEA) followed by a PSA system with a bed of Zeolite 5A .

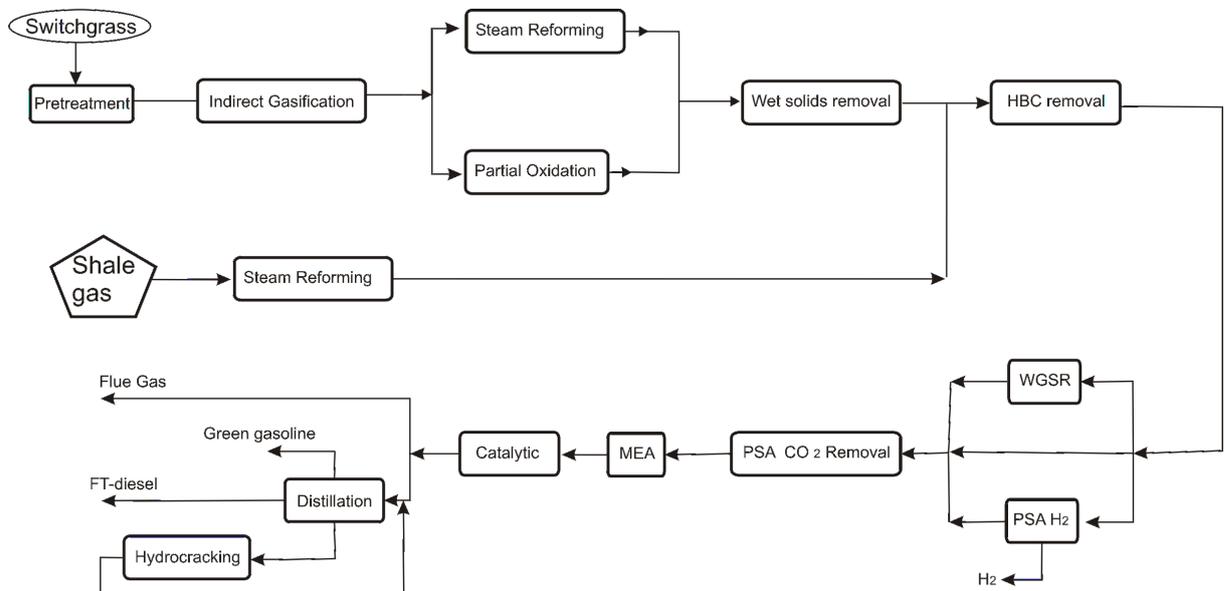


Figure 1.- Superstructure for the production of FT- Diesel from shale gas and switchgrass

Once the gas is purified, the syngas consisting of H_2 and CO follows the Fischer-Tropsch synthesis to produce liquid hydrocarbons using a catalyst of iron or cobalt. The operating conditions are to be optimized (ratio of H_2 and CO and operating temperature at the reactor). The synthetic diesel is produced in addition to gasoline, gas products, and heavy fuels [19]. The optimal operating pressure is assumed to be 30 atm according to experimental results [18].

Finally, the FT liquids produced are separated from the water by gravity separation and refined to different fuels using atmospheric distillation. The heavy products can be hydrotreated to increase the yield to

diesel [20]. The results from Bezerghianni et al. [21] are used to provide a model for the hydrocracking of the heavy oil. Figure 1 shows the superstructure embedding the different alternatives.

3.-Mathematical modelling.

We use reduced order models for the reactors (Shale gas reformer, FT, WGSR and Hydrocracking), mass and energy balances, chemical equilibrium, rules of thumb and design equations. The superstructure is written in terms of the total mass flows, component mass flows, component mass fractions, and temperatures of the streams in the network. The components in the system belong to the set $J = \{ \text{Wa, Met, But, Gasoline, Diesel, Wax, C}_6\text{H}_6, \text{MEA, Tars, CO}_2, \text{CO, O}_2, \text{N}_2, \text{H}_2, \text{H}_2\text{S, NH}_3, \text{CH}_4, \text{C}_2\text{H}_2, \text{C}_2\text{H}_4, \text{C}_2\text{H}_6, \text{SO}_2, \text{C, H, O, S, N, Olivine, Char, Ash} \}$. The details for switchgrass gasification and gas clean up can be found in a previous paper by the authors (Martin & Grossmann 2011). Here we only present a brief description.

3.1.-Switchgrass pretreatment

The pre-treatment stage consists of washing the incoming feed of switchgrass to remove dirt and dust. A small amount of the wash water (1%) is assumed to stay with the feed. It is assumed that 0.5 kg of washing water is needed to wash 1 kg of switchgrass. The washing step takes place at ambient temperature. Then, the grass is partially dried by means of a mechanical press being able to remove 90% of the water that goes with the switchgrass. In order for the gasification to be effective, a reduction in the size of the grass is needed. However, the size required is larger, around 10 mm requiring 30kWh/t [22].

3.2.-Switchgrass gasification

Many different alternatives can be found in the literature for gasification [23]. In this paper we consider only the indirect gasification based on previous results [8] where further details can be found. The switchgrass from the grinding stage enters the gasifier together with steam and a type of sand, olivine, that provides the energy. The gas generated is separated from the solids, mainly char and olivine, in a cyclone. The gas is cleaned in subsequent steps. The solids go to a second chamber, the combustor, where the char is burned to provide the energy to reheat the sand. Due to the fact that the combustion takes place in a different chamber, air can be

used. A make-up of sand is needed. The solids, mainly olivine, are separated from the gases in a cyclone and recycled to the gasifier. The combustion gas is cleaned from ash and cooled down from where energy can be obtained for the process. The model for this system is based on the experimental results by Phillips et al. [24]. Thus, we assume that the gasifier operates at 890°C and 1.6 bar while the combustor operates at 995°C.

3.3.-Hydrocarbon removal

There are two main alternatives for decomposing the hydrocarbons generated during the gasification process, steam reforming and partial oxidation. The first one produces more hydrogen but is endothermic, reducing the energy available within the process for heat integration. Partial oxidation is exothermic, which provides energy for the system but the yield to hydrogen is lower [17,25].

Steam reforming: The reactions taking place are of the form given by eq. (1)-(2). Thus, the mass balances for the different species are given based on the stoichiometric relationships derived from them. We assume that the conversions of the hydrocarbons are given as ($Conv_{CH_4} = 0.8$, $Conv_{C_6H_6} = 1$, $Conv_{Tar} = 1$, $Conv_{C_2H_6} = 0.99$, $Conv_{C_2H_2} = 0.90$, $Conv_{C_2H_4} = 0.90$) and that of the ammonia ($Conv_{NH_3} = 0.90$) as proposed by Philips et al.[24]. The reactions are endothermic. We assume that the reactor operates adiabatically.



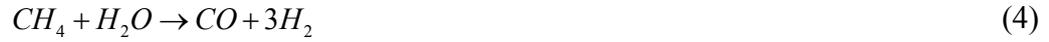
Partial Oxidation: For partial oxidation, pure stoichiometric oxygen is provided to eliminate the hydrocarbons generated in the gasification process, which in turn generates more CO and hydrogen.



The mass balances of the species in the tar are calculated based on the conversions of the hydrocarbons and that of the ammonia following the stoichiometric relationships given by eqs (2)-(3). The conversions of the different hydrocarbons ($Conv_i$) are taken to be the same as in the report by Philips et al. (2007) based on the results by Vernon et al. and Deutschmann & Schmidt [26-27]. The process is exothermic and we assume that it is able to generate steam in order to cool down the equipment.

3.4.-Shale gas steam reforming

The composition of the shale gas (mainly methane, ethane, propane, CO₂ and nitrogen) varies significantly from site to site and even depends on the actual region of the well [28,29]. According to the literature the mean values of the composition are around 95% of methane, 2.7% of ethane and inerts. If we focus on the Marcellus shale up to 97% is methane while nitrogen and ethane add up to the 100% [28] [29]. Thus, for the sake of simplification, we assume that shale gas is mainly methane and the reactions and the equilibrium constants are given as follows [30].



$$kp = 10^{\left[\frac{11650}{T} + 13,076\right]} = \frac{P_{CO} \cdot P_{H_2}^3}{P_{CH_4} \cdot P_{H_2O}} \quad (6)$$

$$kp = 10^{\left[\frac{1910}{T} - 1,784\right]} = \frac{P_{CO_2} \cdot P_{H_2}}{P_{CO} \cdot P_{H_2O}} \quad (7)$$

The atomic balances are as follows:

$$\begin{aligned} mol_{CH_4} \Big|_{in} &= mol_{CH_4} + mol_{CO} + mol_{CO_2} \Big|_{out} \\ 4 \cdot mol_{CH_4} + 2 \cdot mol_{H_2O} \Big|_{in} &= 4 \cdot mol_{CH_4} + 2 \cdot mol_{H_2} + 2 \cdot mol_{H_2O} \Big|_{out} \\ mol_{H_2O} \Big|_{in} &= mol_{H_2O} + mol_{CO} + 2 \cdot mol_{CO_2} \Big|_{out} \end{aligned} \quad (8)$$

Since the first equilibrium depends on the pressure, we use compressor 6, assumed to be a polytropic compressor, to adjust the pressure for the reaction. Due to the fact that the reaction for the steam reforming is endothermic, we have to burn part of the natural gas, separated in Spl3, to provide the energy to keep the temperature constant

$$Q_{prod} = \sum_i fc(i, Tar2, Mix2) * (\Delta H_f + \int_{T_{ref}}^{T_{out}} CpdT) \quad (9)$$

$$Q_{prod} = \sum_{j=entradas} \sum_i fc(i, Tar2, Mix2) * (\Delta H_f + \int_{T_{ref}}^{T_{out}} CpdT) \quad (10)$$

$$Q(Tar2) = (Q_{prod} - Q_{reac}); \quad (11)$$

$$fc(CH_4, Spl3, Tar2) = Q(Tar2) / PCI_{gas}; \quad (12)$$

The gas coming out of the reformer is sent to the purification stage before the PSA system for removal of hydrocarbon traces.

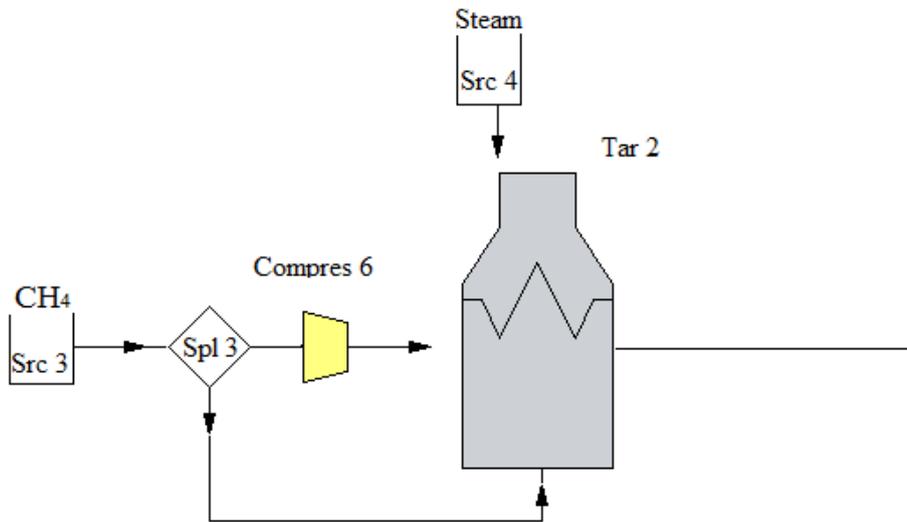


Figure 2.-Scheme of shale gas reforming

3.5.-Clean up

This stage is divided in two. We first eliminate the solids (Ash, Char and Olivine) and NH_3 using a scrubber that operates at 1.2 bar and 40°C requiring 0.25 kg of freshwater per m^3 of gas [31]. The gas leaves the scrubber saturated with water and is prepared for the second stage, a PSA system that works at 25°C and 4.5 bar using silica gel as adsorbent where the last traces of hydrocarbons are eliminated [32]. Thus, we compress the gas assuming polytropic behaviour, and cool it down. Due to the low temperature, water condenses before the PSA adsorption beds and it is discharged. The PSA system is modeled as two beds, one operating and the second one in regeneration to allow continuous operation of the plant.

3.6.-Composition adjustment.

Once the main contaminants are eliminated, the ratio between CO and H_2 may need to be adjusted so that the feed to the FT-reactor is appropriate for the optimal production of the diesel fraction. In order to perform such adjustment, we consider three alternatives. The first one is the use of water gas shift to reduce the amount of CO by producing more H_2 . The second is a simple bypass where the composition remains unchanged. Finally, a hybrid membrane/PSA system is proposed to remove hydrogen based on recent results in the literature [33,34].

Water Gas Shift Reaction (WGSR): The reaction taking place in the water shift reactor is widely known, eq (13):



Its conversion depends on the molar ratio of steam to CO and the operating temperature. Thus, using the experimental data by Choi & Stenger [35] we developed a correlation [36] to predict the conversion as function of both parameters so that the model can be solved in steady state.

Bypass: It may be possible that the stream does not need any adjustment in the CO:H₂

H₂ Membrane / PSA system: The stream to be treated in the membrane / PSA system for the recovery of hydrogen has to be adjusted in terms of temperature, 25 °C, and pressure, 4.5 bar assuming that there is a 10% loss in the previous PSA system. The compression is modelled assuming polytropic behaviour to determine the final temperature and energy required. As a result of the cooling, water condenses. The amount condensed is determined by the saturation conditions of the exiting gas. In this PSA it is assumed that only hydrogen is eliminated from the stream with an efficiency of 100%. The other gases pass through. Finally, all the streams are mixed adiabatically.

3.7.-CO₂ removal

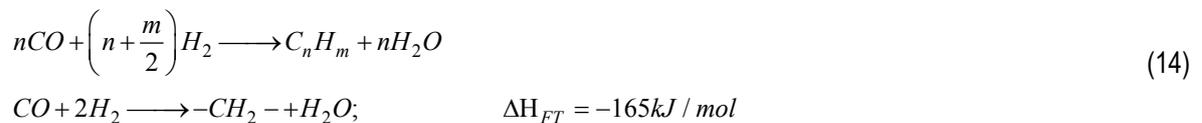
The removal of CO₂ and H₂S is the last cleaning stage for the preparation of the syngas. According to the results by Wang et al [18], the optimal pressure for diesel is 30 bar. This fact, together with the negative effect of the H₂S for the catalytic reaction and the results from a previous paper [8] defines the clean-up of the gas as follows: the first stage is the PSA for the removal of CO₂, and next the MEA absorption which provides with the proper pressure for the Fischer-Tropsch reactor. Therefore, the gas is first treated in a PSA system to remove CO₂ by adsorption on Zeolite 5A or 13X [37,38]. The operating conditions are 25 °C and 4.5 bar. Thus, the stream is compressed and cooled down. In this process water condenses too. The amount of water condensed is given by the saturation conditions of the exiting gas, while the water vapor accompanying the CO₂ is absorbed too. The cycle is short and the absorption capacity is around 0.1kg of CO₂ per kg of zeolite allows the removal of 95% of the CO₂. The outlet of the PSA system must be further treated for the removal of H₂S.

Typically MEA systems operate at 29 °C and elevated pressure, 29 bar [24,39,40-42]. The sour gas is placed into contact adiabatically with the MEA (fresh and regenerated) in a contact column adiabatically. The heat of reaction heats up the exiting streams. The liquid stream is treated to recover the amine in a distillation column, while the gas can be directed to the synthesis. Due to the required increase in the pressure, a two-stage

compression system with inter cooling is proposed. Thus, the temperature after each of the compressors and the energy required are calculated assuming adiabatic behavior with inter-cooling. Once the gas is at the desired pressure, it has to be cooled down to 29 °C. Thus, condensation is likely. The water is eliminated to avoid the dilution of the solution of MEA. The characteristics of the solution of MEA needed to remove the CO₂ and H₂S are taken from GPSA [39]. The recoveries of sour gases are 0.9 and 1 for CO₂ and H₂S, respectively. The gas phase coming out of column 1 is calculated based on the separation efficiencies. The MEA with the sour gas is treated in a distillation column to regenerate and recycle the amine, while the sour gases leave the column from the top. The operation of this column is based on the experimental data and design conditions provided by the literature [39-42]

3.8.-Synthesis

The gas from treatment must be heated up to the appropriate temperature, $T_{\text{synthesis}}$. The temperature and the ratio of CO and H₂ must be optimized for the correct distribution of fractions. The general agreement for describing the mechanisms of the synthesis of liquid fuels is a stepwise chain growth where the formation of higher hydrocarbons occurs through the dissociation of carbon monoxide so that the surface species (at first, surface carbon) have the option of desorbing to produce an alkene, or to be hydrogenated to desorb as an alkane, or to continue the chain growth process by adding another CH₂. There are a number of reactions that are undesirable such as the production of methane from syngas, or Boudouard equilibrium. The valuable reaction is given by eq. (14) which is the most dominant reaction when using cobalt-based FT catalyst, while in case of iron-based catalyst, the WGSR also takes place enabling the operation at a lower temperature.



The operating conditions depend on the types and quantities of Fischer-Tropsch products desired, ranging from either low (200–240 °C) or high (300–350 °C) temperatures, and pressures from 10 to 40 bar employing either cobalt or iron based catalysts. Currently iron based catalysts are used operating at high temperatures for the production of gasoline and small hydrocarbons, while either cobalt based or iron based catalyst that operate at low temperature (200–240 °C) are used for the production of diesel or heavier products [20]. However, the iron catalyst provides high selectivity for C₁₀ – C₁₈, which means a high yield of diesel.

Moreover, the reactions with iron catalyst are usually conducted at 30 bar, which is convenient due to the fact that the MEA treatment is already operating at that pressure, and thus, is the catalyst of choice. Furthermore, Fischer-Tropsch synthesis requires careful control of the H₂:CO ratio to satisfy the stoichiometry of the synthesis reactions, as well as to avoid deposition of carbon on the catalysts (coking). While some reviews like van der Laan & Beenkakers [43] and recent experimental by studies [18,44] report that the production of gasoline and diesel is enhanced for H₂/CO ratios from 1 to 2 and for optimal production of the diesel fraction. Some researchers report a minimum ratio of 1.7 for iron catalysts [20]. In order to assess the effect of the uncertainty we decide to impose 1.7 as lower bound for the ratio H₂/CO. To determine the operating conditions we assume that the Fischer-Tropsch reactor operates as a polymerization reactor whose product distribution is given by the Anderson-Schulz-Flory (ASF) distribution [43,46,47]. The fraction of mass of the hydrocarbons $i = \text{number of C}$, w_i , depends on the probability of chain growth, α . A conversion of 0.9 in CO is considered based on the results by Park & Norbeck [48]. According to the literature [49], α is a function of the temperature, and the ratio CO to H₂ through eqs. (15)-(16) determine w_i .

$$w_i = \alpha^{i-1} (1 - \alpha)^2 \cdot i \quad (15)$$

$$\alpha = \left(0.2332 * \left(\frac{y_{co}}{y_{H_2} + y_{co}} \right) + 0.633 \right) * \left(1 - 0.0039 * ((T_{\text{Synthesis}} + 273) - 533) \right) \quad (16)$$

We consider five main products from the distribution, C₁-C₂, C₃-C₄, gasoline, diesel and heavy products whose fraction is calculated from eq. (15) and the reactor outlet is calculated based on them.. The distribution is to be optimized for the production of FT-diesel.

3.9.-Separation and hydrotreatment.

Fischer-Tropsch liquids can be refined to renewable (green) gasoline, diesel fuel, and aviation fuel depending on the process conditions. The gas fractions are separated from the liquids by flash separation. In order to avoid losing liquid, the flash operates at the same pressure of the reactor, but the mixture is cooled down to 30°C. We assume that we recover the gases and small hydrocarbons but not the liquids, gasoline, diesel, wax and water. The gases could be further separated into methane and butane fractions, or can be used together as

flue gas to produce energy. For the economic analysis, we assume for simplicity that the gases are used as flue gas since its purification to be sold as products or to be recycled is expensive and not the objective of the paper.

The three liquid fuel fractions are separated in an atmospheric distillation system. We heat up the feed to 220°C. Typically these towers have 30 trays and the working temperatures are 125 °C for the top (Gasoline), 220 °C for the diesel and 280 °C at the bottom [50]. The reflux ratio is assumed to be 2 to be on the conservative side [51]. There is no reboiler, but steam is directly injected and the energy consumption is due to the production of that steam, 0.18 kg of steam per kg of residue to be on the safe side [51-54]. The bottoms of the column are treated to obtain more diesel using hydrocracking, since it avoids the presence of aromatics in the diesel [20]. Based on the literature, we assume that only 7.5% of the hydrogen is fed to the reactor, 600 ft³ of hydrogen per bbl, remains with the products [50]. To model the yield of the hydrocracking reactor we use the experimental data for the conversion and selectivity as a function of the temperature from the paper presented by Bezergianni et al. [21] to develop a reduced order model given by (17)-(18).

$$X_{R3} = 0.000185714 \cdot (T_{\text{reactor3}})^2 - 0.128829 \cdot T_{\text{reactor3}} + 22.6931 \quad (17)$$

$$S_{\text{diesel}} = -0.00014286 \cdot (T_{\text{reactor3}})^2 + 0.099514 \cdot T_{\text{reactor3}} - 16.383 \quad (18)$$

The products of the hydrocracking are cooled down to 30 °C in a flash so that the liquids (gasoline, Diesel and heavy fractions) are recycled to the column to be separated while the excess of hydrogen is recycled back to the reactor.

3.10.-Solution procedure.

The original MINLP problem is decomposed into 2 NLP's subproblems, whether the raw syngas generated at the gasifier is either partial oxidized or follows steam reforming. Each NLP, consisting of around 5,500 equations and 6,200 variables, is solved to optimize the production of synthetic diesel determining the operating conditions to be used at the shale gas reformer, the operating pressure and the fraction of gas used to maintain adiabatic operation, the WGSR, the Fischer-Tropsch reactor and the hydrocracking unit. The objective function to be maximized is given by a simplified manufacturing cost involving the production of diesel and hydrogen and the energy and raw materials consumption. We assume a selling price of diesel of \$1 /kg for the objective function.

$$Z = (fc(\text{Diesel}) \cdot 1) - P_{\text{Steam}} \cdot (Q_{\text{Pre-WGSR}} + Q_{\text{Pre-FT Reactor}} + \text{Steam}_{\text{WGSR}} + \text{Steam}_{\text{SR}}) +$$

$$P_{Hy} \cdot (fc(H_2) - 0.01 \cdot fc(Wax) \cdot 1.58) - P_{Elect} \sum_i W_{Compressor,i} - P_{Shale} fc(Shale) - P_{Biomass} fc(Biomass) \quad (19)$$

Thus, the main decision variables are the operating pressure and steam ratio at the shale gas reformer, the split fraction at the water gas shift reactor and hydrogen PSA system for the composition adjustment, the water gas shift operating conditions (temperature and amount of steam needed), the operating conditions in the Fischer-Tropsch reactor (temperature and CO/H₂ ratio), and the temperature at the hydrocracking unit.

Next, for each optimization run, heat integration within the process is performed using SYNHEAT [55] to design the heat exchanger network for the optimal reuse of the excess of energy, while minimizing the cooling needs of the facility. Finally, a detailed economic evaluation based on Sinnott's procedure [8, 56] (Martin & Grossmann, 2011; Sinnott, 1999) is carried out involving equipment cost, maintenance, chemicals and utilities, management, labour and raw materials cost.

We follow this procedure for a number of price levels for switchgrass (30 to 200 \$/t), shale gas (0.5 to 5 times the base price of \$4.6MMBTU, the stable one for natural gas before the impact of the shale gas [57], so that the range captures the current price), hydrogen (0.5 to 1.5 the basis, \$1.6/kg), with fixed or variable availability of biomass, variable availability of Shale gas up to 50% or 100% of the availability of biomass for a total of more than 100 experimental runs.

4.-Results.

In order to evaluate the different scenarios and technological alternatives (the reforming processes), a detailed cost analysis is performed involving raw material cost, maintenance, cost of utilities and chemicals, labor, annualized equipment cost and the cost for the management of the facility, following Sinnott's method [56]; see also previous papers by the authors for further details on equipment pricing [8]. The prices for utilities are updated from the literature (\$0.019/kg Steam; \$0.057/ton cooling water [57], \$0.06/kWh [59] \$0.021/kg Oxygen [60]. The generation of an excess of steam in the heat integration stage is considered as a revenue of \$0.0077/kg_{steam} [61].

4.1.-Technology selection

The basic idea is that the production cost of FT diesel from switchgrass [16] has higher production cost compared to biodiesel and bioethanol via gasification of switchgrass and the investment is far larger than that for a biodiesel production facility [8, 10, 16]. Thus, we propose the use of shale gas to not only increase the

production capacity of liquid fuels, but also reducing the production costs to make it competitive with second generation of bioethanol and biodiesel.

In this section we compare two technologies, steam reforming and partial oxidation of the gas generated at the gasification of the switchgrass for different levels of shale gas availability to decide on the technology of choice. Based on a previous paper by the authors [16] the use of partial oxidation results in lower yield to liquid biofuels. To avoid that the natural gas be devoted to the production of hydrogen increasing the profitability of the process but with a lower yield to synthetic liquid fuels, we fix the minimum capacity of the plant that operates using partial oxidation to be at least 85% of the liquid fuel capacity obtained when using steam reforming since our aim is to help reduce the dependency on liquid fossil fuels.

Figures 3 and 4 show the distribution of products and the biofuel yield (in mass percentage) for the use of steam reforming, while Figures 4 and 5 present the same variables but for the use of partial oxidation. We see that in general steam reforming of the raw syngas from the gasifier provides higher yields while the only small advantage is a slightly higher production of hydrogen in case of partial oxidation. If we compare the production costs, see Figure 7, steam reforming is cheaper when biomass is the main raw material. As the ratio biomass/shale gas reaches 2 both technologies results in similar production costs take to the same values. Beyond this ratio, partial oxidation is more profitable. However, the idea of using shale gas as a complementary source suggests the use of steam reforming. At this point, due to the uncertainty in selling the flue gas obtained, we did not consider it as an extra credit in terms of revenue.

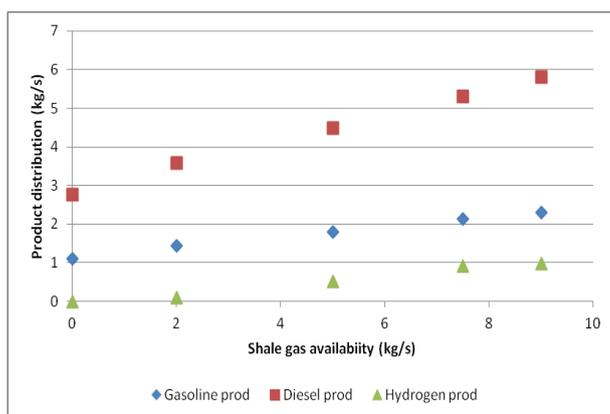


Figure 3 Product distribution SR

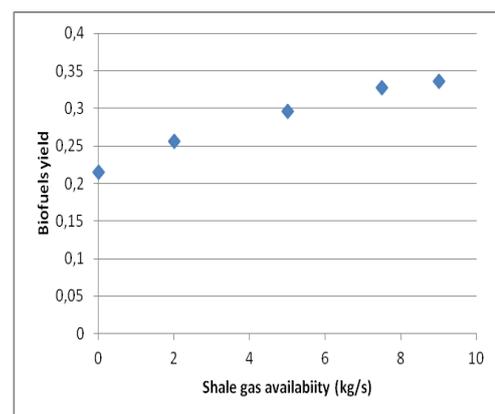


Figure 4. Bio fuel yield (SR)

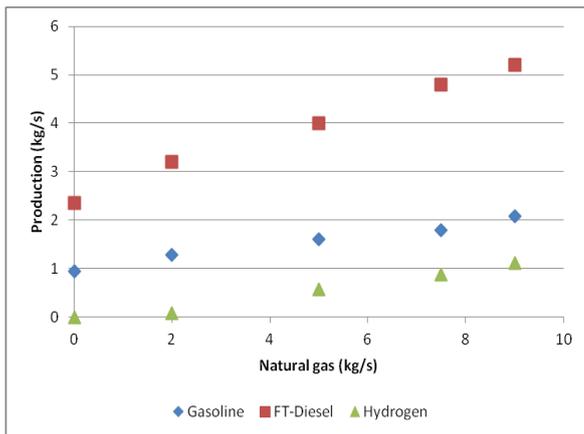


Figure 5 Product distribution (PO)

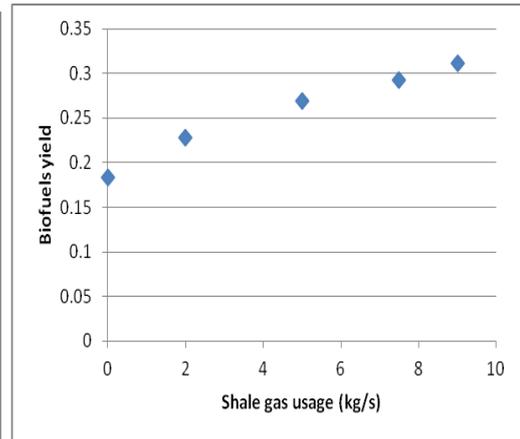


Figure 6 Bio fuel yield (PO)

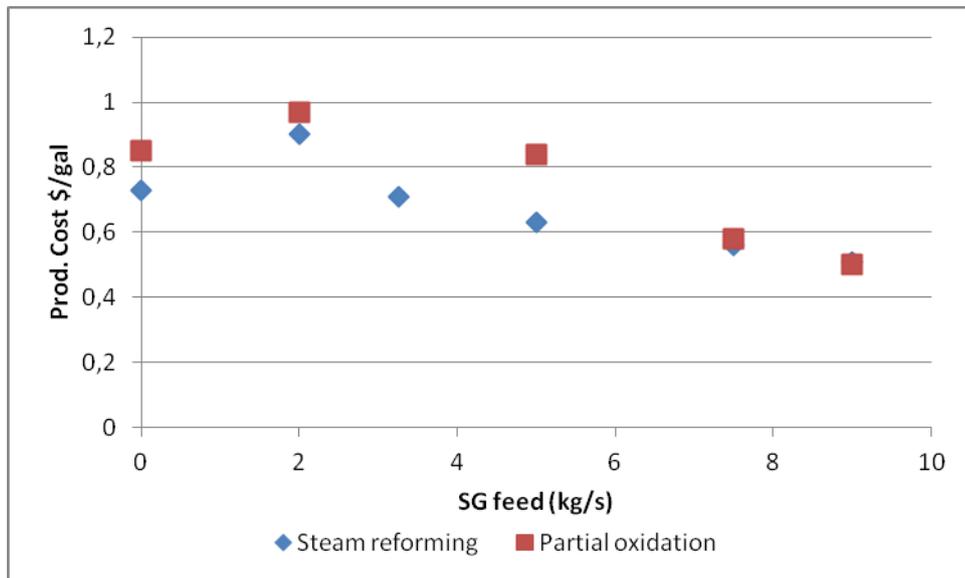


Figure 7. Effect of the shale gas feed to the production cost.

4.2.- Sensitivity analysis

The highest yield to biofuels and hydrogen provides an advantage for the steam reforming of the gas coming from the gasifier to help substitute the use of crude oil as source of fuels for the automotive industry. Thus, we focus on this option to evaluate the effect of the prices of the raw materials, biomass and shale gas, the price of the byproduct hydrogen, as well as the availability of shale gas and biomass. Since our aim is to produce liquid fuels in a sustainable way, the idea is to use shale gas to complement the biomass as raw material and thus serve as a bridge between fossil fuels and bio-based ones. We divide this section in three parts. The first deals with fixed biomass feedstock to be used where we use the shale gas, depending on its price, to complement the production of liquid fuels and hydrogen. In the second section we allow the optimization to decide on the amount of biomass to be used depending on its price and the price of the shale gas finally in

section 3 we allow larger availability of shale gas up to 1:1 the maximum availability of the biomass as an extreme case. Needless to say, this last case is the less sustainable of the three.

1.- Fixed biomass feedstock.

We use shale gas to increase the production of diesel substitutes to the production capacity of most bioethanol plants, around 60MMgal/yr. This value corresponds to the typical size of a bioethanol facility based on the lignocellulosic material. We evaluate the simultaneous production of liquid fuels and hydrogen for a fixed flow of biomass, 18kg/s, a feasible harvesting and processing capacity whose yield is not enough to reach the desired liquid fuels production level (Martín & Grossmann 2011). We consider a variable feedstock of shale gas, with a maximum availability of up to 50% of the biomass on a mass basis. The main idea is for the Shale gas to be a complement increasing the liquid fuels production while reducing the dependency on fossil fuels. In all cases we found a liquid fuel distribution of 71% of FT-diesel and 29% of green gasoline. To facilitate the presentation of the results, we divide them by evaluating the effects of the shale gas, the biomass and the hydrogen byproduct.

a) Effect of biomass and shale gas cost on the production level and cost

In Figure 8 we present the effect of the price of shale gas and biomass on the production of hydrogen and the usage of shale gas. For low shale gas prices, all the available shale gas is used and the excess not needed to meet the liquid fuels demand is devoted to the production of hydrogen. As the price increases, we can find a breakpoint beyond which the use of shale gas is decreased while at the same time the hydrogen production is also reduced. As the biomass cost increases the shale gas price at which hydrogen production is cut decreases. This breakpoint point is interesting because for current biomass cost (\$30/t to \$50/t) it matches the natural gas cost before the shale gas was found or exploited. As both raw material prices increases, the system will only meet the demand of liquid fuels with no net hydrogen production.

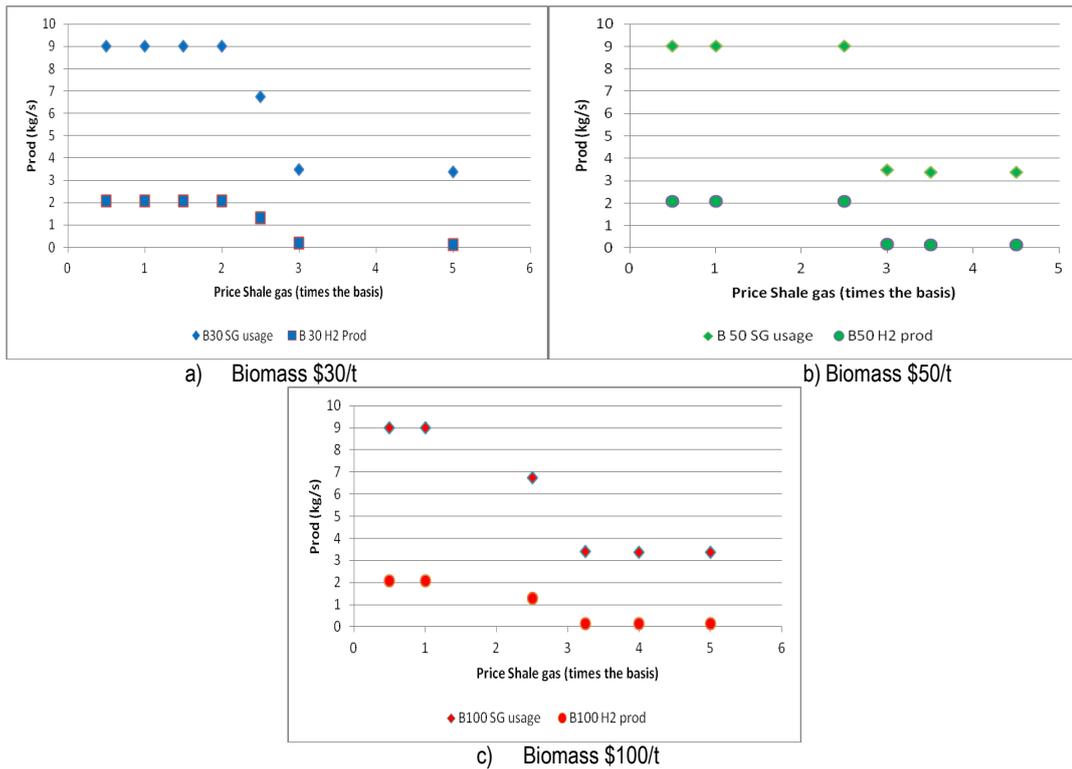


Figure 8 Effect of shale gas and biomass prices effect on the usage of shale gas and hydrogen production

b) Effect of the price of hydrogen

Another interesting variable is the price of hydrogen. If the hydrogen price is around \$1.58/kg, from 0.5 to 1.5 times this value (with biomass and shale gas at base prices) we see that there is no effect on the consumption of shale gas. Hydrogen is a valuable byproduct, and therefore as much of it should be produced, (see Figure 9).

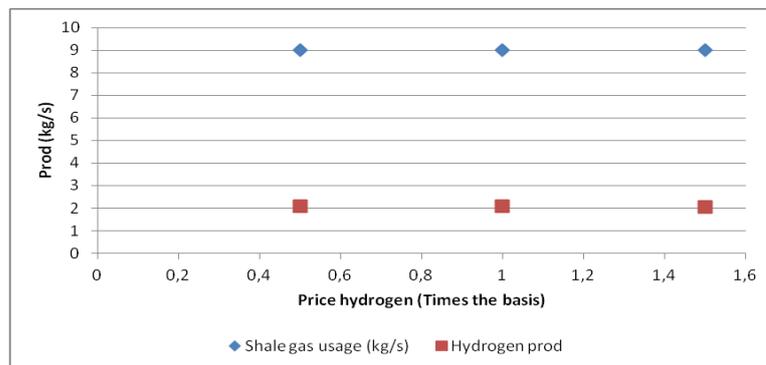


Figure 9 Effect of hydrogen price on its production and shale gas usage.

c) Effect of the demand on liquid fuels.

At this point we want to evaluate the responsiveness of the plant to a fluctuation in the demand of liquid fuels. Thus, in this case we vary the production level of liquid fuels from 45MMgal/yr to 90MMgal/yr for fixed availability of biomass (18kg/s), and for variable availability up to an extra 50% contribution from shale gas (9kg/s). In Figure 10 we see that the production of gasoline increases linearly with that of FT-diesel while the hydrogen production decreases. The reason is that the resources are used to produce the liquid fuels instead of hydrogen in order to meet the demand. In mass percentage, the increased demand of liquid fuels increases the mass ratio yield to biofuels from the raw materials (the sum of biomass and shale gas), see Figure 11. This means that the production of hydrogen is accompanied with the extra production of CO₂, and thus the total yield when producing the hydrogen decreases since a larger portion of the raw material is lost as CO₂. However, the high value of the hydrogen is what drives the production of hydrogen if there is raw material availability. For all the cases the ratio of FT-diesel in the liquid fuels production remains constant at 71%.

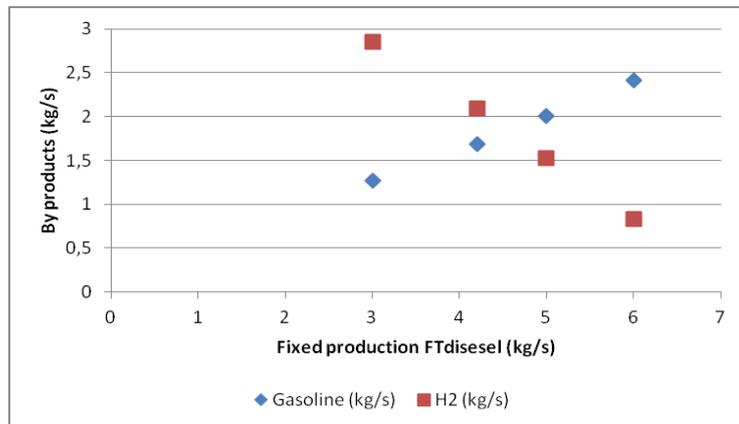


Figure 10 Production of byproducts as function of the production of FT-Diesel

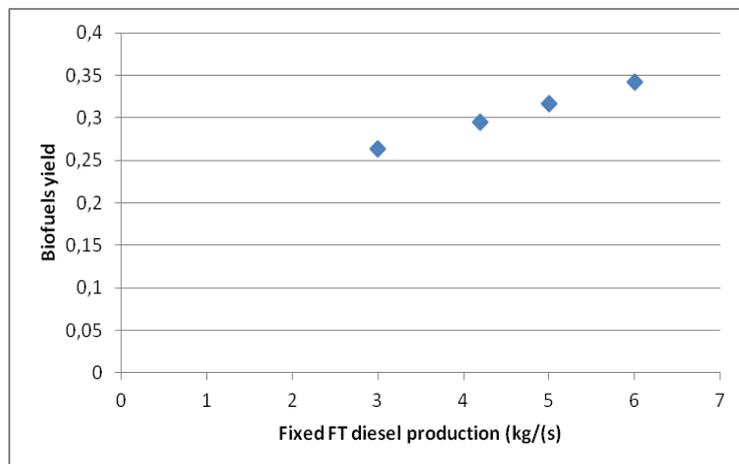


Figure 11. Biofuels yield for different FT-diesel production levels

The production cost of liquid fuels increases as the shale gas increases. This is due to the fact that as long as the shale gas lies below the value of \$11.5/MMBTU, the excess that is not needed to meet the liquid fuels demand is devoted to the production of hydrogen. However, as the shale gas prices increases, we only use that which is required to meet the liquid fuels demand, reducing the production of hydrogen and increasing the production cost, see Figure 12. In this figure we have not consider the flue gas as credit, but it will reduce the production cost by 35-50% of the one shown on the Figure 12.

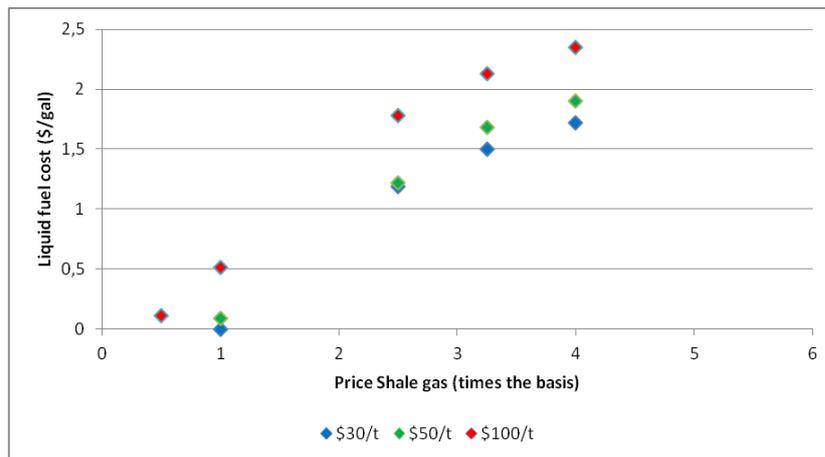


Figure 12.- Cost of liquid fuels

2 Variable usage of the biomass.

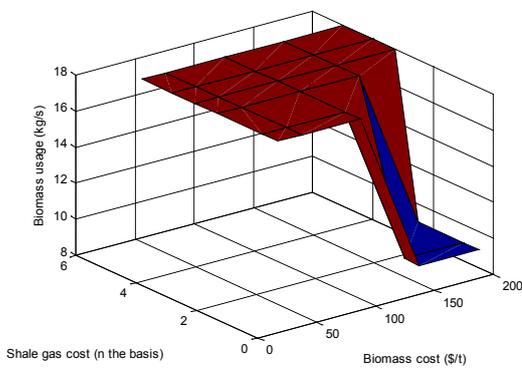
For this section we do not fix the amount of biomass to be used but we allow that the prices of the main raw materials, biomass and shale gas, decide on the raw material to use to meet the demand of liquid fuels.

a) Fixed production level of liquid fuels

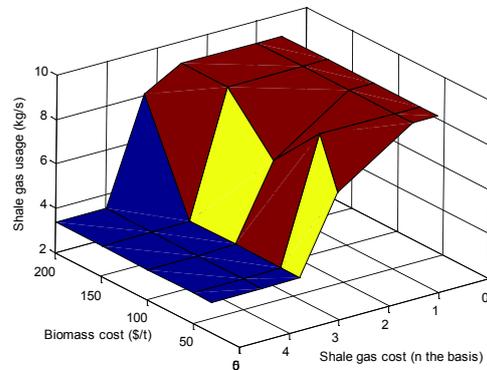
As reported in the literature the biomass price is volatile due to its changing yearly availability. Thus, our next study evaluates the relative usage of raw materials in order to produce a fixed rate of liquid fuels, 60MMgal/yr (FT-diesel & green gasoline), with variation in the prices of the raw material. In this case we allow the production cost of biomass to reach \$200/t together with the fact that the biomass usage may be variable, up to 18kg/s, while the shale gas usage can reach 50% of the maximum availability of biomass (9kg/s) from \$2.3/MMBTU.

As we can see in Figure 13 a), the full capacity of biomass is used unless it reaches a cost higher than \$150/t and the shale gas price is kept to the current levels. In the Figure 13 we can see that the biomass use is at the maximum unless the cost reaches \$150/t in which case the system tries to increase the yield of total fuels by

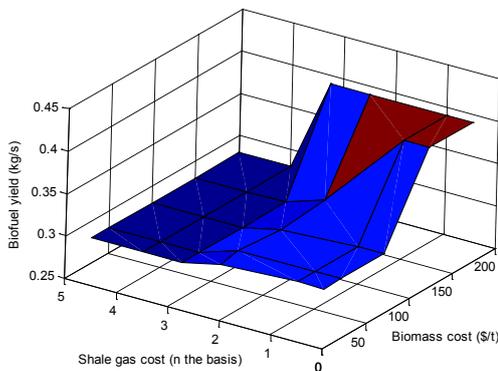
reducing the hydrogen production. In general, the usage of shale gas to meet the demand decreases with its cost and for around the price previous to the discovery of the shale gas, a minimum amount of it is recommended to meet the demand. Figure 13 b) shows that shale gas is used to its full availability until it reaches a price of 2 or 3 times the base price. From Figure 13 d) it can be seen that the hydrogen production decreases since we are meeting the demand of liquid fuels, while the extra raw material is used for the production of hydrogen. However, hydrogen production is attractive only for shale gas prices up to 3 times the base price of shale gas. With the increase in the cost of biomass, the system evolves into increasing the mass yield towards total quantity of fuels produced, as long as the shale gas cost is not high. While for the highest costs for both raw materials, the production is reduced to meet the demand, see Figure 13 c). Finally the production cost of the liquid fuels, see Figure 13 e), increases almost linearly with that of the raw materials and to keep a production cost below \$1/gal we need to assure shale gas costs are not higher than twice the base value and biomass costs below \$75/t. In this price we have not included the contribution of the flue gas. In Figure 13 f) we see that by selling the flue gas we can get an extra credit of up to \$1.5/gal discount in the best of the cases and we can keep production prices for liquid fuels below the \$1/gal target if at least one of the raw materials maintain its price at base levels.



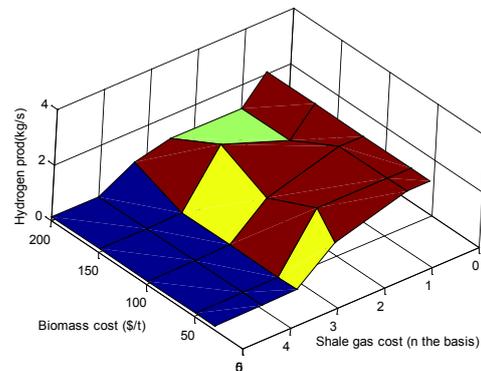
a) Biomass Usage



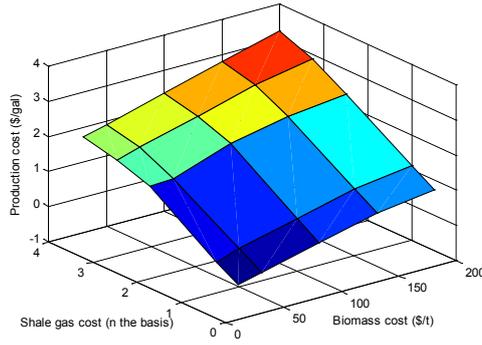
b) Shale gas Usage



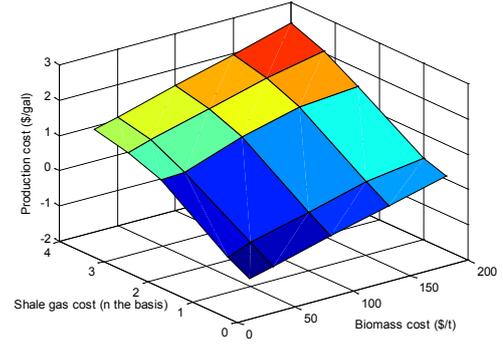
c) Biofuel yield



d) Hydrogen production



e) Liquid fuels production cost (No flue gas)

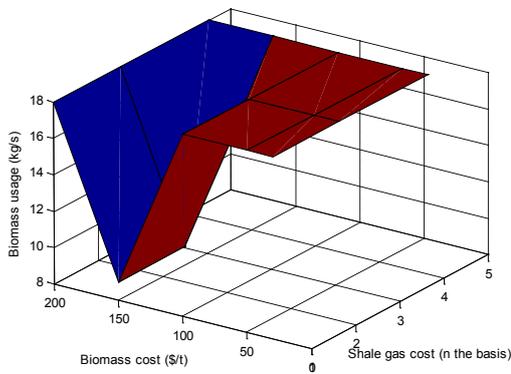


f) Liquid fuels cost with flue gas credit

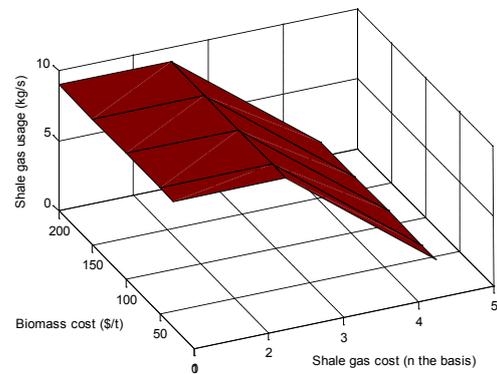
Figure 13 Usage of shale gas and biomass for fixed production of liquid fuels

b) Variable production level of liquid fuels.

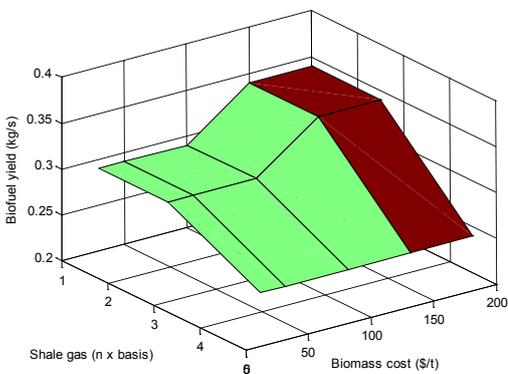
For this analysis we evaluate the effect of the prices of the raw materials, the biomass and shale gas prices, for a fixed price for hydrogen on the production level of diesel and hydrogen and on the selection of the raw material to use. We allow a range of liquid fuels production from 45 MMgal/yr to 60MMgal/yr with raw materials availability of 18kg/s of biomass and up to 9kg/s of shale gas. See Figure 14.



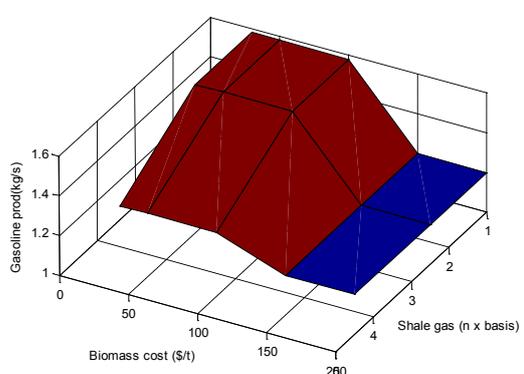
a) Biomass Usage



b) Shale gas usage



c) Biofuels yield



d) Gasoline production

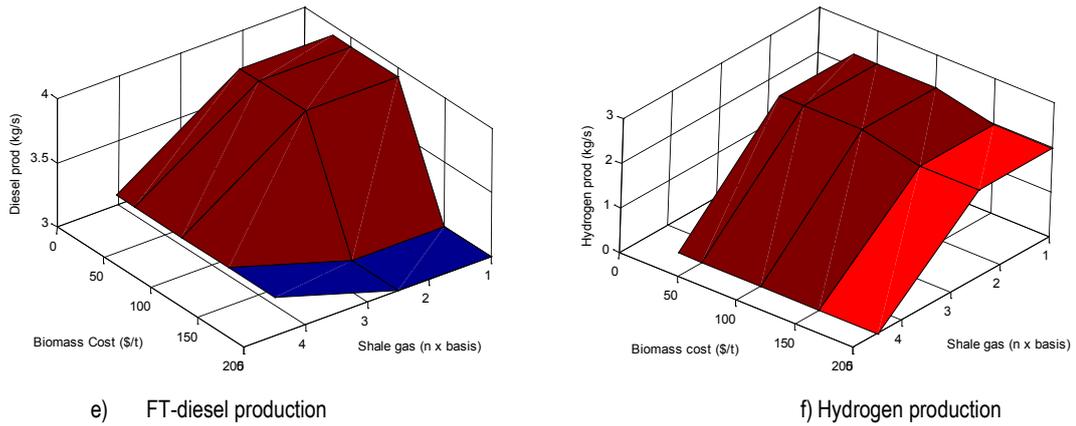


Figure 14 Usage of shale gas and biomass for variable production of liquid fuels

The biomass price becomes important in the decision for the product distribution beyond \$100/t where the biomass availability is not fully used. However, if it reaches the value of \$200/t the increase in the yield to liquid fuel results in the fully use of the biomass (14.a), together with the fact that as the shale gas price increases (14.b) the usage of shale gas is no longer recommended. Therefore, as the price of biomass and shale gas increase, the productivity of fuels, the total yield from the raw material to fuels, no matter whether they are liquid or hydrogen, becomes a major decision variable (14.c). Thus, the raw materials are used to meet the demand of FT-diesel and gasoline while hydrogen is produced only if the shale gas price is low (14.d-e).

3.-Increased availability of shale gas.

Finally, we allow the usage of biomass to vary from 9 to 18 kg/s, while the availability of shale gas can reach also 18kg/s. This means that we only provide 50% replacement of the fossil fuels in terms of mass ratio fed. Under these conditions we evaluate the effect of the price of the renewable and non renewable raw materials on the production facility for a fixed production level of 60MMgal/yr of biofuel, see Figure 15.

Only if the biomass goes over \$100/t and the shale gas remains at the price of \$4.6/MMBTU or below, the maximum availability of the biomass is not used and shale gas is preferred instead. This occurs at a lower biomass cost than in the previous cases due to the availability of the shale gas. However, for this case the dependency on fossil fuels is larger. As soon as the price for shale gas increases, the option for biomass is clear to maintain the production capacity (16.a), while the usage of shale gas decreases as its price increases (16.b). Finally, the lower the price of the shale gas is the higher the production of hydrogen, which means that shale gas

is helping reach the $H_2:CO$ ratio that the FT reactor requires. Apart from that, it is mainly devoted to the production of hydrogen also increasing the production of CO_2 .

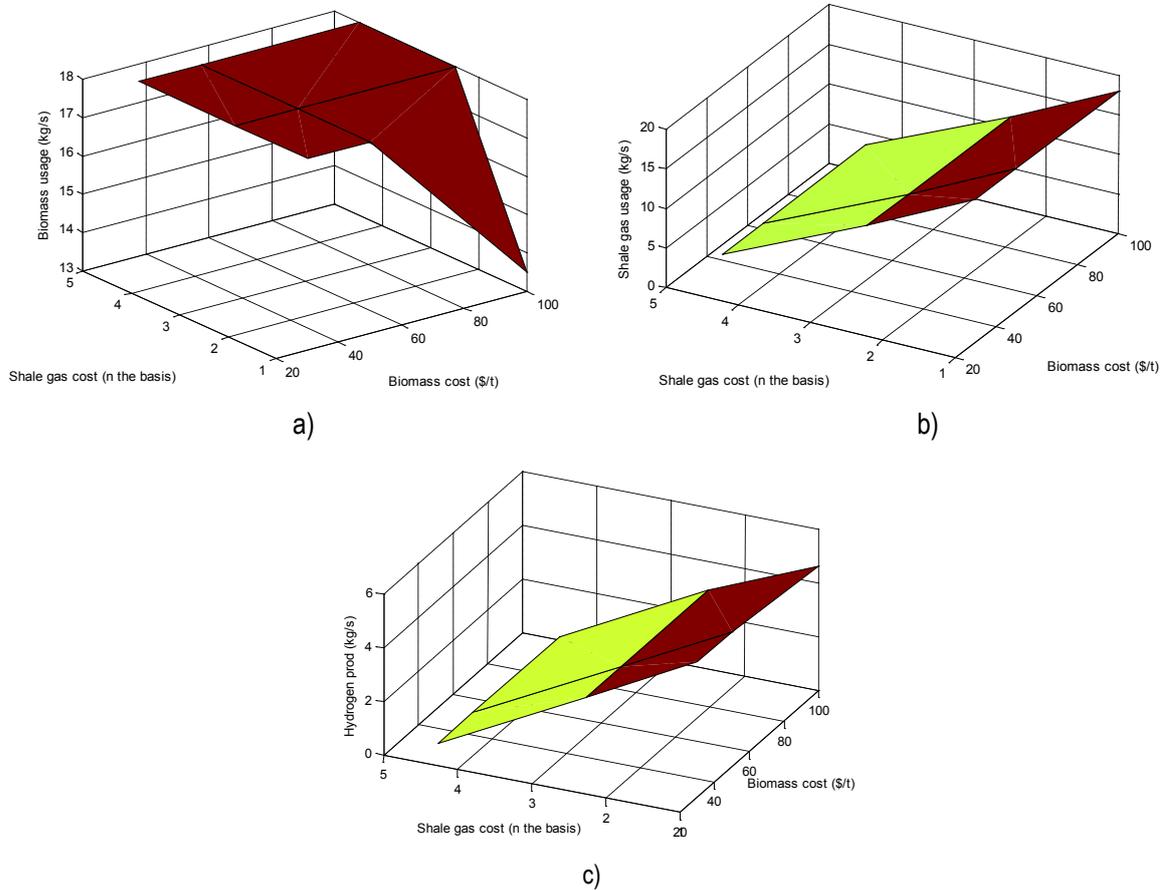


Figure 15. Usage of shale gas and biomass for fixed production of liquid fuels. 100% availability of shale gas

6.-Conclusions

We have addressed in this paper the conceptual optimal design of Fischer-Tropsch diesel from lignocellulosic switchgrass and shale gas to increase the yield to liquid fuels. We have proposed a superstructure that considers as major decisions the type of reformer and the use of fossil raw material such as shale gas. Next, we evaluated the process to determine the main operating conditions at the reformer, the FT reactor and the hydrocracking unit for the optimal production of the diesel fraction, while performing a sensitivity study involving the raw materials and by product (hydrogen) prices, on the product distribution and raw material usage.

Biomass price becomes critical above \$100/t at which point the usage of shale gas increases to meet the demand, while the use of shale gas is not interesting when its price goes beyond \$11.5/MMBTU. Below

these prices for the raw materials, we can obtain liquid fuels at the target production cost of around \$1/gal and for shale gas prices below \$5/MMBTU, which is the current scenario. Beyond those limiting values the production cost of the synthetic liquid fuels is no longer competitive with completely fossil fuel based gasoline or diesel. Hydrogen will be produced to help in the economy of the plant as long as there is raw material available to meet the demand for liquid fuels and the shale gas price is low, since the excess of shale gas is typically devoted to the production of hydrogen. Furthermore, the target price of \$0.41/gal obtained for bioethanol (Martin & Grossmann 2011a) can be obtained either if we consider the flue gas as profit or the prices of switchgrass and shale gas are below \$125/t and \$2.8MM/BTU, respectively, so that there is a large contribution of shale gas and a large amount of hydrogen is produced.

Acknowledgments

The authors gratefully acknowledge funding from the NSF Grant CBET0966524 and the Center for Advanced Process Decision-making at Carnegie Mellon University.

7.-Nomenclature.

α	chain length	
$fc(j, \text{unit1}, \text{unit2})$	individual mass flow rate from unit1 to unit2 (kg/s)	
$fc(j)$	individual mass flow of final product j	
$F(\text{unit1}, \text{unit2})$	mass flow rate from unit1 to unit2 (kg/s)	
P_i	Price of component i (\$/unit)	
Steam_i	Steam consumed at different equipment (kg/s)	
Q_i	Energy to preheat the stream entering equipment i (kJ/s)	
S_{diesel}	Selectivity to diesel	
S_{gasoline}	Selectivity to gasoline	
$T_{\text{Synthesis}}$	Temperature at FT reactor	(°C)
T_{reactor3}	Temperature at hydrocracking	(°C)
$T(\text{unit1}, \text{unit2})$	Temperature of the stream from unit 1 to unit 2	(°C)
X_{R3}	Conversion of reactor 3 (Hydrocracking)	
W	Work (kJ/s)	

7.-References.

- 1 Cucek, L., Martín, M., Grossmann, I.E., Kravanja, Z. Integration of Process Technologies for the Simultaneous Production of fuel Ethanol and food from Corn grain and stover. *Comp Chem Eng* 2011; 35 (8): 1547-1557
- 2 Agrawal, R., Singha, N.R., Ribeiro, F.H., Delgass, W.N., Perkis, D.F., Tyner, W.E. Synergy in the hybrid thermochemical–biological processes for liquid fuel production. *Comp Chem Eng* 2009; 33: 2012–2017
- 3 Liu, G., Larson, E.D., Williams, R.H., Kreutz, T.G., Guo, X. Making Fischer-Tropsch Fuels and Electricity from Coal and Biomass: Performance and Cost Analysis. *Energy Fuels* 2011; 25: 415–437

- 4 Baliban, R.C., Elia, J.A., Floudas, C. A. Simultaneous process synthesis, heat, power, and water integration of thermochemical hybrid biomass, coal, and natural gas facilities. *Comp Chem Eng* **2012**. doi:10.1016/j.compchemeng.2011.10.002
- 5 <http://www.tradingeconomics.com/commodity/-natural-gas> (last seen April 2012)
- 6 <http://geology.com/energy/shale-gas>.
- 7 Sumi. L. Shale Gas:Focus on the Marcellus Shale. for the oil & gas accountability project/ earthworks, MAY 2008
- 8 Martín, M., Grossmann, I.E. Energy optimization of lignocellulosic bioethanol production via gasification *AIChE J* 2011; 57(12): 3408- 3428
- 9 Martín, M., Grossmann, I.E. Energy Optimization of Bioethanol Production via Hydrolysis of Switchgrass *AIChE J*. 2012; 58(5): 1538-1549
- 10 Martín, M., Grossmann, I.E. (2012) Simultaneous optimization and heat integration for biodiesel production from cooking oil and algae. *Ind. Eng. Chem Res* **DOI:** 10.1021/ie2024596
- 11 Jarvis E.E. (2008) Aquatic Species Program (ASP): Lessons Learned <http://www.nrel.gov/biomass/pdfs/jarvis.pdf> (last accessed June 2012)
- 12 http://www.exxonmobil.com/Corporate/energy_vehicle_algae.aspx (last seen June 2012)
- 13 Teles, U.M., Fernandes, F.A.N. Hydrocracking of Fischer – Tropsch Products. Optimization of Diesel and Nafta Cuts. *Chem Biochem Eng Q* 2008; 22: 227-231
- 14 Kim, Y.H., Jun, K.-W., Joo, H., Han, C., Song, I.K. A simulation study on gas-to-liquid (natural gas to Fischer-Tropsch synthetic fuel) process optimization, *Chem Eng J* 2009; 155 (1-2): 427-432
- 15 Swanson, R.M., Platon, A., Satrio, J.A.; Brown, R.C. Techno-economic analysis of biomass-to-liquids production based on gasification. *Fuel* 2010; 89 (Suppl. 1): S11-S19
- 16 Martín, M., Grossmann, I.E. Process optimization of FT- Diesel production from biomass. *Ind Eng Chem Res* 2011b; 50 (23):13485–13499
- 17 Rand, D.A.J., Dell, R.M. Hydrogen Energy Challenges and Prospects The Royal Society of Chemistry, Thomas Graham House, Science Park, Milton Road, Cambridge CB4 0WF, UK ISBN: 978-0-85404-597-6. 2008.
- 18 Wang, Y., Fan, W., Liu, Y., Zeng, Z., Hao, X., Chang, M., Zhang, C., Xu, Y., Xiang, H., Li, Y. Modeling of the Fischer–Tropsch synthesis in slurry bubble column reactors. *Chem Eng Process* 2008; 47: 222–228
- 19 Opdal O. Skreiberg O. Production of synthetic biodiesel via Fischer-Tropsch synthesis Biomass-To-Liquids in Namdalen, Norway Project report by Olav A. Opdal Department of Energy & Process engineering Faculty of Engineering Science and Technology Norwegian University of Science and Technology. 2006
- 20 Dry, M.E. The Fischer–Tropsch process: 1950–2000. *Catal Today* 2002; 71: 227–241
- 21 Bezergianni, S., Kalogianni, A., Vasalos, I. A. Hydrocracking of vacuum gas oil-vegetable oil mixtures for biofuels production. *Bioresour Technol* 2009; 100: 3036–3042
- 22 Mani, S. , Tabil, L.G., Sokhansanj, S. (2004) Grinding performance and physical properties of wheat and barley straws,corn stover and switchgrass. *Biomass Bioener* 2004; 27: 339 – 352

- 23 Bridgwater, A.V. Renewable fuels and chemicals by thermal processing of biomass. *Chem Eng J* 2003; 91: 87–102
- 24 Phillips, S., Aden, A., Jechura, J. and Dayton, D., Eggeman, T. Thermochemical Ethanol via Indirect Gasification and Mixed Alcohol Synthesis of Lignocellulosic Biomass. Technical Report, NREL/TP-510-41168, April 2007
- 25 Brenes, M.D. Biomass and bioenergy Nova Science Publishers, Incorporated ISBN-13: 9781594548659. 2006
- 26 Vernon P.D.F., Green, M.L.H., Cheetham, A.K., Ashcroft, A.T. Partial oxidation of methane to synthesis gas *Catal Lett* 1990; 6(2): 181-186
- 27 Deutschmann, O., Schmidt, L.D. Two-dimensional modeling of partial oxidation of methane on rhodium in a short contact time reactor Twenty-Seventh Symposium (International) on Combustion/The Combustion Institute, 2283–2291. 1998.
- 28 George, D.L. Bowles, E.B. Shale gas measurement and associated issues. *Pipe and Gas J.* 2011, 238 (7) <http://www.pipelineandgasjournal.com/shale-gas-measurement-and-associated-issues?page=show> (last accessed March 2012)
- 29 Bullin, K.A., Krouskop, P.E. (2009) Compositional variety complicates processing plans for US shale gas, *Oil and Gas Journal.* 107, 10. <http://www.ogj.com/articles/print/volume-107/issue-10/special-report/compositional-variety-complicates-processing-plans-for-us-shale-gas.html>
- 30 Roh, H-S., Lee, D.K., Koo, K.Y., Jung, U.H., Yoon, W.L. Natural gas steam reforming for hydrogen production over metal monolith catalyst with efficient heat-transfer. *Int J Hydrogen* 2010; 35 (3): 1613-1619
- 31 Martelli, E., Kreutz, T., Consonni, S. Comparison of coal IGCC with and without CO₂ capture and storage: Shell gasification with standard vs. partial water quench *Energy Procedia* . 2009; 1: 607-614
- 32 Olofsson, I., Nordin, A., and Söderlind, U. Initial Review and Evaluation of Process Technologies and Systems Suitable for Cost-Efficient Medium-Scale Gasification for Biomass to Liquid Fuels *Ingemar* ISSN 1653-0551 ETPC Report 05-02. 2005
- 33 Neves, C. F. C, Schvartzman, M.M. A.M Separação de CO₂ per meio da tecnologia PSA *Quim. Nova*, 2005; 28: 622-628.
- 34 Choi, D., Chipman, D. C., Bents, S.C., Brown, R. C. A Techno-economic Analysis of Polyhydro-xyalkanoate and Hydrogen Production from Syngas Fermentation of Gasified Biomass *Appl Biochem Biotechnol* 2010; 160(4):1032-1046.
- 35 Choi, Y., Stenger, H. G. Water gas shift reaction kinetics and reactor modeling for fuel cell grade hydrogen *J. Power Sources* 2003; 124: 432–439
- 36 Martín, M., Grossmann, I.E. Energy optimization of Hydrogen production from biomass. *Comp Chem Eng* 2011c; 35 (9): 1798-1806
- 37 Ko, D., Siriwardane, R., and Biegler, L.T. Optimization of a Pressure-Swing Adsorption Process Using Zeolite 13X for CO₂ Sequestration. *Ind Eng Chem Res* 2003; 42 (2): 339-348
- 38 Reynolds, S., Ebner, A., Ritter, J. (2005) New Pressure Swing Adsorption Cycles for Carbon Dioxide Sequestration. *Adsorption*, 2005; 11 (Suppl. 1): 531-536

39 GPSA Engineering_Data_Book FPS VERSION 21-10. 2004

40 Nexant Inc. Equipment Design and Cost Estimation for Small Modular Biomass Systems, Synthesis Gas Cleanup, and Oxygen Separation Equipment Task 2: Gas Cleanup Design and Cost Estimates – Black Liquor Gasification Subcontract Report NREL/SR-510-39944 May 2006

41 Nexant Inc. Equipment Design and Cost Estimation for Small Modular Biomass Systems, Synthesis Gas Cleanup, and Oxygen Separation Equipment Task 9: Mixed Alcohols From Syngas — State of Technology Subcontract Report NREL/SR-510-39947 May 2006

42 Nexant Inc. Equipment Design and Cost Estimation for Small Modular Biomass Systems, Synthesis Gas Cleanup, and Oxygen Separation Equipment Task 2.3: Sulfur Primer Subcontract Report NREL/SR-510-39946 May 2006

43 van der Laan, G.P., and Beenackers, A.A.C.M., Kinetics and selectivity of the Fischer-Tropsch synthesis: a literature review. Catal Revs Sci Eng 1999; 41: 255-318

44 Mazzone, L.C.A., Fernandes, F.A.N. Modelling of Fischer – Tropsch synthesis in tubular reactor. Latin Am Appl Res 2006; 36: 141-148

45 Schulz, H., Schaub, G., Claeys, M., and Riedel, T. Transient initial kinetic regimes of Fischer-Tropsch synthesis App Cat A 1999; 186: 215-227.

46 Fürsinn, S., Ripfel, K., Rauch, R., Hofbauer, H. Diesel aus Holz - Die FS Synthese als zukunftsweisende Technologie zur Gewinnung flüssiger Brennstoffe aus Biomasse, 4. Internationale Energiewirtschaftstagung an der TU Wien, 2005

47 Yuan W., Vaughan G.C., Roberts C.B., Eden M.R. Modeling and Optimization of Supercritical Phase Fischer-Tropsch Synthesis, Computer Aided Chemical Engineering, 2011; 29B: 1929-1933.

48 Park C. S. and Norbeck J. M. Synthetic diesel production from Carbonaceous Feed Stocks. 2009
www.eri.ucr.edu/ISAFXVCD/ISAFXVAF/SyDPCFS.pdf

49 Hyun-Seob, S., Ramkrishna, D., Trinh, S., Wright, H. Operating Strategies for Fischer-Tropsch Reactors: A Model-Directed Study, Korean J Chem 2004; 21: 308-317.

50 Speight, J.G. The Chemistry and Technology of Petroleum. 2nd Edition. Marcel Dekker Inc., New York. 1991.

51 Parkash, S. Refining Process Handbook. Gulf Professional Publishing Elsevier. 2003

52 Jones, D.S.J. Pujadó, P. R. Handbook of petroleum processing. Springer. 2006.

53 Marcel-Dekker Encyclopedia of Chemical Processing and Design, 1997

54 More, R.K., Bulasara, V. K., Uppaluri, R., Banjara, V. R. Optimization of crude distillation system using Aspen Plus: Effect of binary feed selection on grass-root design. Chem Eng Res Des 2010; 88: 121–134

55 Yee, T.F., Grossmann, I.E. Simultaneous optimization models for heat integration – II. Heat exchanger networks synthesis. Comp Chem Eng 1990; 28: 1165-1184.

56 Sinnott, R.K. Coulson and Richardson, Chemical Engineering. 3rdEd. Butterworth Heinemann, Singapur. 1999

57 <http://www.wtrg.com/daily/gasprice.html> (Aug 2011)

58 Franceschin, G., Zamboni, A., Bezzo, F., Bertucco, A., Ethanol from corn: a technical and economical assessment based on different scenarios. *Chem Eng Res Des* 2008; 86 (5): 488-498

59 Balat, M., Balat, H., Öz, C. Progress in bioethanol processing. *Prog Energy Combust Sci*, 2008; 34 (5): 551-573

60 Forsberg, C. W. Gorenssek, M.B. Relative Economic Incentives for Hydrogen from Nuclear, Renewable, and Fossil Energy Sources American Institute of Chemical Engineers Annual Meeting Salt Lake City; November 4–9, 2007

61 Smith, R., Varbanov, P. What's the price of Steam? *CEP*, 2005, July 29-33