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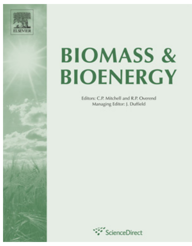

Plant design aspects of catalytic biosyngas conversion to higher alcohols

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ABSTRACT

Although biomethanol production has attracted most of the attention in the past years, there is a current trend for the synthesis of higher alcohols (i.e. ethanol, plus C_3–C_4) from biomass gasification. These compounds could be used directly as fuel or fuel additives for octane or cetane number enhancement. These also serve as important intermediates for the chemical industry. In this paper a comparison is performed between the different process configurations a higher alcohols production plant from biomass gasification can take. These options are modelled in Aspenplus™; all steps and important unit operations are presented with the aim to correctly evaluate the peripheral energy requirements and conclude with the overall thermodynamic limitations of the processes. The differentiation between black liquor and solid biomass gasification, the type of catalyst employed, and the effect of the recycling scheme adopted for the reutilization of unreacted syngas are evaluated. The design has to cope with the limited yields and poor selectivity of catalysts developed so far. The gas cleaning is different depending on the different requirements of the catalysts as far as H_2S purity. The process modelling results reveal that the hydrogenation of CO to higher alcohols is favoured by high pressure, temperature around 325 °C and high reactor residence times. A biorefinery using modified Fisher–Tropsch (FT) catalysts (MoS_2) prevail over modified MeOH catalyst (Cu–Zn based) for HA production. The efficiency of HA production in HHV terms can reach up to 25%.

1. Introduction

Coal, lignite, oil and natural gas have been used over 100 years both in the power and chemicals production industry and have been the prime energy sources of the global economy. Important issues such as climate change, reduced fossil fuel resources, coupled with increased prices lead to efforts to supplement fossil fuels consumption by renewable biomass resources, which are abundant and unexploited. The realignment of the chemical industry from a petrochemical refining based to a biorefinery based has attracted a lot of attention and the feasibility of this concept has become a national goal of many countries [1].

Bioethanol is the most common 1st generation biofuel, currently being produced from the fermentation of sugars i.e. using edible biomass as feedstock. Gasification of biomass to synthesis gas (H_2/CO), followed by catalytic conversion of syngas, could produce significant amounts of ethanol, plus higher alcohols that could be used as additives into transportation fuels without competing with the food sector. The

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latter is a second generation biofuel approach and is regarded by many as a way to reduce the amount of carbon dioxide released into the atmosphere by replacing part of fossil and thus higher CO_2 footprint energy sources [2–5]. Except from the production of methanol and ethanol, and Fischer–Tropsch liquids' potential uses in automotive sector [6], extensive research efforts have been focused in the production of higher alcohols (HA: C_2–C_4 alcohols), and in the development of active and selective catalysts [7–10]. The resulting alcohols mixture could be used directly as fuel, as fuel additives for octane or cetane enhancement, as oxygenate fuel additives for environmental reasons, and as intermediates to form other fuel components as well as for the production of solvents or other chemical sub-processes in the chemical industry. HA gained ground against other bioliquids, because they have a wide range of uses as final products or as key intermediate components for the chemical industry. The most common HA alcohol is ethanol (CH_3CH_2OH). Apart from being a fuel already produced by 1st generation biofuel routes, it has major industrial uses such as its conversion by oxidation into acetaldehyde (CH_3CHO). It is also used in the preparation of various derivatives, such as ethyl chloride, in plastics production etc. As a fuel, it is suitable for internal combustion engines (ICE) [6]. The next HA is propanol, and its principal use is in the production of acetone, which is used extensively as a solvent and as a starting compound in the manufacture of numerous other organic compounds. Butanol is claimed to have good qualities for direct replacement of gasoline [11]. Even higher HAs are produced in large quantities and they have a wide range derivatives used in the production of resins, paints, polyester fibres and other applications [12,13].

The biorefinery concept focuses on replacing the resources currently used (mainly natural gas) to transform biological raw materials into industrially useful intermediates up to end products. The production of HA in a biorefinery application could involve two different pathways: the first one is the biochemical conversion of biomass derived sugars though alcoholic fermentation (adopted in Brazil and the United States). The second route is via thermochemical conversion of biomass which offers a more effective means for the recovery of the energy content of biomass in a direct way and shorter times. Important thermochemical processes used for the production of highly energetic gaseous fuel are: (a) pyrolysis achieved in the absence of oxidant and (b) gasification, i.e. the thermal decomposition and reaction of biomass occurring with the help of an oxidant such as pure oxygen or air (autothermal process) or steam (allothermal) to yield a combustible gas rich in carbon monoxide and hydrogen [7–10].

In the present work, an energetically self-supported biorefinery section is designed for two different feedstocks: i.e. woody biomass and the pulp and paper industry by-product: black liquor. The latter is one of the largest concentrated biomass sources available in regions with many large pulp and paper industry units (i.e. northern Europe, etc.). Since the pulp industry has already tackled the logistics of handling huge amounts of wood it is more likely that their by-product is used apart from producing energy in recovery boilers, for the production of biofuels. Nevertheless, the production of syngas from solid biomass is a primary future target in case of the absence of an existing relevant industry. In all cases a biorefinery has to function without any requirements for energy above the levels its primary feedstock can cover. This study describes in detail the entire sub-processes and simulation methodologies in Aspenplus™ process simulation tool. A detailed bibliographical search is performed into works employing this software for the evaluation of biorefinery operations based on syngas [14–18].

The modelled sections are the gasification (both black liquor and solid biomass), the oxygen production, the gas cleaning and removal of acid gas components and finally the production of HA (in two different cases fashions depending on the catalyst employed). The envisaged process could well function from sizes of 100 to 400 MW thermal input of biomass [19], with the first being the basis for the calculations.

2. Process description

A simplified flow diagram for the process is shown in Fig. 1. Both wood based circulating fluidized bed gasification and black liquor gasification are shown in cases (a) and (b). All major processing steps for the conversion of wood or black liquor to syngas via oxygen gasification are apparent: the air separation unit, the gas-cleaning system and the catalytic synthesis of HA. Each process area in the scheme is described below.

2.1. *Air separation unit*

A cryogenic separation unit is required in order to produce a highly pure oxygen stream. Cryogenic distillation separates oxygen from air by liquefying at low temperatures. Ambient air is compressed in three stages via a compressor with intercooling and further cooled with chilled water. Residual water vapour, carbon dioxide, and atmospheric contaminants are removed in molecular sieve adsorbers. The cooling of air to cryogenic temperatures is achieved by heat exchanger and the required cooling loads derive from the already cold product streams. Such a configuration can reach to an oxygen purity of up to 98% [20]. For further oxygen purification, an extra column for argon separation would be required.

2.2. *Gasification*

Over the past decades many different gasifier types have been developed. Nevertheless for the sizes of a biorefinery operation i.e. well over 30 MW thermal input, only two technologies have the maturity to be considered for current or near future application. A circulating fluidized bed (CFB) gasifier is recommended for solid fuels with diverse textures and moisture levels. If the biomass is in the form of liquid (such as in black liquor) or solid without serious problems and energetic requirements for its partitioning down to fine particles (<1 mm), then an entrained flow system can also be considered.

Gasifying woody biomass in circulating fluidized beds and black liquor in entrained flow gasifiers has many differences in operating conditions, quality of produced gas etc. The typical chemical analyses of both fuels adopted are presented in Table 1. Primarily, the gasification temperature in a CFB is below 1000 °C compared to entrained flow reactors that surpass this (up to 1200 °C) [13,21]. Most of the times, entrained