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Chemical Engineering Research and Design

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# Thermally integrated bio-syngas-production for biorefineries

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## ABSTRACT

Maximising the thermal efficiency of a biorefinery is a major challenge in the production of economically competitive biomass-based chemicals. This paper compares different bio-syngas to methanol routes with respect to their energy demands and proposes a novel heat integration concept.

Previous studies on biorefineries have tended to focus on the chemical transformations involved. The defunctionalisation of biofeedstocks required to eliminate the excess oxygen they contain is also a very energy-consuming process, which exerts a considerable influence on the overall yields which can be achieved. In this article we deal with the less appreciated issue of thermal integration by analysing two principle routes for the generation of 'bio'-synthesis gas for methanol synthesis: a conventional high temperature biomass gasification process and a scheme based on aqueous-phase reforming (APR). Low temperature gasification processes below 250 °C, such as APR, permit one to use the heat liberated in the methanol synthesis for the endothermic synthesis gas production step. The composition of the resultant synthesis gas must be modified slightly to meet the demands of the methanol synthesis reaction using a low temperature retro-water-gas shift reaction in a special adsorptive reactor. The results indicate that the low temperature arrangement has an edge in terms of the net energy consumption for a given methanol production and the analysis reveals topics of interest for future research in this area.

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**Keywords:** Biorefinery; Thermal integration; Synthesis gas; Aqueous-phase reforming; Methanol synthesis

## 1. Introduction

The depletion of fossil fuel reserves makes it necessary to find alternatives for both energy generation and the production of organic chemicals. The use of biomass has been proposed as a promising, environmentally compatible and sustainable solution to both problems. Whilst there are a variety of other options available for energy generation, e.g. atomic, solar and wind power, biomass alone can serve as a carbon source for the production of chemicals once fossil fuels are exhausted. It is thus necessary to develop new industrial manufacturing processes for chemicals based on renewable resources.

The amounts of biomass required provide a further argument for its use in chemical production rather than for energy generation. Fig. 1 illustrates that the overwhelming proportion of fossil fuels is used for the generation of electrical and thermal energy or in the transport sector, whilst a relatively

small fraction is employed for chemical production. Since the amount of agricultural or other suitable land available for biomass harvesting is limited and must also serve the needs of food production, it can be easily calculated that it is unfeasible to meet even the present demands for energy production using biomass-based fuels, even using second generation lignocellulosic biofuels. On the other hand the use of renewable biomass resources for the chemical industry is a much more viable proposition, offering little competition to other land use needs. Of the 11,050 m<sup>2</sup> of usable land available pro capita in 2050, woefully inadequate for energy requirements, it has been estimated that around 400 m<sup>2</sup> would suffice to cover the needs of chemical production (Pfennig, 2007).

The National Renewable Energy Laboratory (NREL, 2008) has designated the biorefinery concept, analogous to today's petrochemical refineries, as the most promising approach for the production of biomass-based chemicals. Biorefineries use

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Received 13 October 2008; Received in revised form 24 February 2009; Accepted 5 March 2009

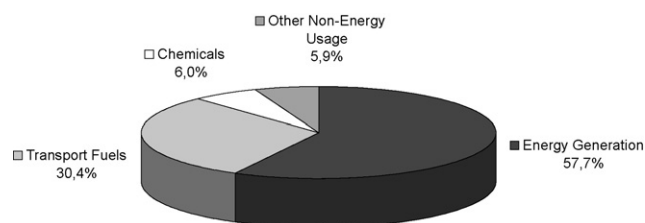


Fig. 1 – Consumption of fossil fuels in 2006 (IEA, 2008).

physical, chemical, biological and thermal treatments and processes to fractionate and transform the biomass into platform chemicals that can be used for biobased commodity chemical production (Kamm et al., 2006). Due to the high functional nature of the molecules present in the biomass, all these processes have the elimination of unwanted functional groups as a common objective.

There are two major strategies for defunctionalising biomolecules. The first is to breakdown the biomass partially into its underlying building blocks, a concept which has the advantage of exploiting the natural synthesis potential available. Werty and Petersen (2004) have identified 12 attractive building blocks for the further synthesis of high-value biobased chemicals. Even so, the resulting molecules still often have to be defunctionalised further prior to their use for commodity chemical production and their integration into established chemical manufacturing network structures is a daunting challenge.

The second strategy is to transform the biomass completely into the  $C_1$  feedstock synthesis gas. On one hand this concept has the disadvantage that a lot of energy is needed to rupture carbon chains, which must then be reconstructed with considerable effort in the subsequent synthesis and processing steps. On the other hand this technique represents a relatively straightforward front-end substitution yielding a feedstock that can be used for conventional thermochemical syntheses in existing plants to produce a wide variety of commodity chemicals. Moreover synthesis gas or syngas generation is perhaps more appropriate for decentralised biomass processing and can be easily transported over pipelines to larger plants for further conversion. As a consequence of these advantages many biorefinery concepts incorporate syngas generation, either as a major pathway in its own right or as an essential component of defunctionalisation strategies (Kamm and Kamm, 2007).

Depending on the raw material, pyrolysis, gasification or steam reforming are commonly used to manufacture biosyngas. The problem with such endothermic processes is the high temperature level required for conversion using conventional technologies. A low temperature process would be more suitable for thermal integration with downstream exothermic processing steps, such as methanol synthesis (MS) or Fischer–Tropsch-synthesis (FTS). Today's petrochemical plants face a similar predicament: the initial functionalisation of alkanes to carbon monoxide or alkenes in steam reformers or steam crackers necessitate temperatures of around 900–1000 °C, which can only be provided through the combustion of by-products or some of the fossil fuel feedstock itself. This represents a considerable sacrifice in terms of yields and efficiencies and requires costly heat-integrated reactor systems.

Fig. 2 depicts the temperature levels required for various processes generating synthesis gas from biomass. It can be recognised, that the operating temperatures for pyroly-

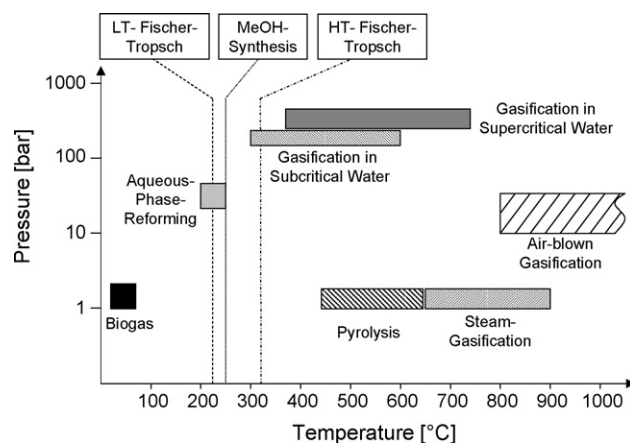
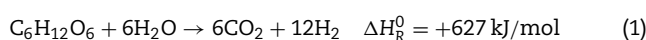


Fig. 2 – Temperature levels of various syngas generation processes.

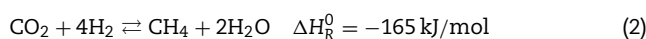
sis, gasification and steam reforming lie well above those of the typical chemical processes for converting synthesis gas to chemical. A direct thermal coupling between the exothermic MS or FTS and the endothermic synthesis gas generation is thus not possible. The heat of reaction needed for pyrolysis or gasification therefore has to be supplied externally by combustion as in the conventional petrochemical plants described above. Ideally, providing the heat required for synthesis gas generation directly from the heat of reaction liberated by the MS or FTS could permit drastic improvements in the overall efficiency of biomass utilisation. From Fig. 2 it can be seen that the only gasification process enabling an expedient thermal integration of this kind is that of aqueous-phase reforming (APR).

Cortright et al. (2002) have demonstrated, that carbohydrate monomers can be converted under relatively mild conditions (225 °C, 30 bar) in the presence of a catalysts into carbon dioxide and hydrogen by means of APR. Supported Pt/Al<sub>2</sub>O<sub>3</sub> or Raney NiSn, which suppress the chemically undesirable methanation reaction, can be used as catalysts (Davda et al., 2005; Shabaker et al., 2004). Since the reaction takes place in the liquid phase, the energy-intensive evaporation of any water present can be dispensed with in APR, making it especially suitable for the gasification of moist biomass. A further advantage is that the gas is generated at higher pressure, thus saving the compression energy that would otherwise be need for most downstream processing. The major disadvantage of APR is that it is only able to convert the carbohydrate monomers derived from cellulose and hemicellulose and, in contrast to high temperature gasification, it cannot process the substantial lignin fraction of the biomass. A pre-treatment, hydrolysis and fractionation of the biomass would thus be necessary before APR could be applied (Huber and Dumesic, 2006).

By way of an example, the APR of glucose, the constituent monomer of cellulose, can be considered as a benchmark:



Methanation occurs as an unwanted consecutive side-reaction:



In order to be able to use the synthesis gas produced in the methanol or Fischer–Tropsch syntheses, it is necessary to

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