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A comparative thermodynamic evaluation of bioethanol processing from wheat straw☆

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HIGHLIGHTS

- Alternative routes to sustainable biofuels from wheat straw have been appraised.
- Thermodynamic analysis has been employed to evaluate four bioethanol processes.
- The *Net Energy Value* of each production path or route was determined.
- Exergetic efficiencies were estimated for the different processes.
- Process *improvement potentials* were then calculated on a comparative basis.

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ABSTRACT

The thermodynamic implications of different bioethanol production routes from wheat straw (a cellulosic co-product or 'waste' stream) have been evaluated. Comparative thermodynamic (energy and exergy) analysis gives rise to alternative insights into the relative performance of various process chains. Energy analysis of four different production paths were firstly analysed via the consideration of mechanical work, temperature changes and separating techniques. The *Net Energy Value* (NEV) of each production path or route was then evaluated, including the effect of system boundary expansion. In contrast, the thermodynamic property known as 'exergy' reflects the ability of undertake 'useful work', but does not represent well heating processes. Exergetic efficiencies were consequently obtained via chemical and physical exergy calculations, along with some of the electrical inputs to the different processes. The exergetic 'improvement potentials' of the process stages were then determined using the exergetic efficiencies and irreversibility values respectively. These estimates will enable industrialists and policy makers to take account of some of the ramifications of alternative bioethanol production routes in a low carbon future.

1. Introduction

1.1. Background

'Biomass', 'bioenergy' or 'biofuels' are produced from organic materials, either directly from plants or indirectly from, for example, agricultural waste products. They can be characterized in two broad categories: woody biomass [including forest products, *short rotation coppice* (SRC, e.g., willow), or untreated wood products] and non-woody biomass [including high energy crops (e.g., rape, sugar cane, and maize), animal waste, and waste from food processing]. Carbon dioxide (CO_2) released when energy is generated from biomass is roughly balanced by that absorbed during the fuel's production. It is thus regarded as a 'carbon neutral' process, and its use offers the opportunity to help meet CO_2 reduction targets. Energy crops and agricultural residues are consequently considered to be good candidates for next generation of renewable energy technologies. However, fossil fuels are used during their production (embodied in fertilizers), and during cultivation, transportation and processing. So that bioenergy resources are not quite as low carbon as would otherwise be the case. In any event, biomass can be refined to produce a biofuel, which would help to meet the *United Kingdom of Great Britain and Northern Ireland* (UK) and *European Union* (EU) targets to gradually replace a proportion of fossil fuels in transport with biofuels.

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The UK transport sector has the fastest rate of growth in terms of primary (and end-use) energy consumption, and is currently responsible for 30% of UK CO_2 emissions. Hammond et al. [1] recently suggested that there is only a modest potential for biofuel use in the UK automotive sector. Indeed, the IEA 'technology roadmap' on transport biofuels [2] suggested that, although *First Generation Biofuels* (FGB) will dominate the global market up to 2020 (Hammond and Li [3]; in line with the OECD-FAO projections previously analysed by Hammond and Seth [4]), advanced or *Second Generation Biofuels* (SGB) might constitute some 75% of biofuels production by 2050. Such SGB are generally produced from agricultural or crop 'wastes' (such as straw) and from non-food energy crops, which significantly reduces their negative impacts. The IEA [2] argued that the amount of global biofuels for transport could rise nearly sevenfold over the period 2020–2050 [to just over 30 ExaJoules (EJ) equivalent primary energy demand *per annum*]. That would represent some 27% of global transport fuel supply by the middle of the 21st Century in contrast to only about 2% today [2,5]. Bioethanol – a bio-based substitute for petroleum or 'gasoline' – produced from wheat straw could yield 6.8% of total world fuel supplies if all current cars were fitted with E85 ready engines: a blend of petroleum (or 'gasoline') and denatured bioethanol, containing up to 85% of the latter. These bioethanol projections [2] indicated that conventional bioethanol from sugar beet and corn would begin to grow slowly after 2015, although it would be replaced rather more rapidly by advanced bioethanol production from sugarcane and cellulosic feedstock after about 2020.

1.2. Wheat straw as a bioethanol feedstock

Straw is an agricultural by-product; the dried stalks of cereal plant, after the grain and chaff have been removed. These stems arise from crops (such as barley, oats, rice, rye or wheat) that can alternatively be fed to animals ('fodder'), used as a layer on the ground for cattle and other livestock to lie on ('bedding'), or for the making traditional objects (e.g., straw baskets or hats). Glithero et al. [6], for example, recently estimated the potential supply of cereal straw as a lignocellulosic SGB feedstock via an on-farm survey of 249 farms (cereal, general cropping and mixed units) in England – the largest geographic part of the island of *Great Britain* (GB) which accounts for some 84% of the UK population. This study was linked with data from the English *Farm Business Survey* (FBS), which is conducted on behalf of the UK *Department for Environment, Food and Rural Affairs*. Glithero et al. [6] consequently found that there is a potential cereal straw supply of about 5.27 million tonnes (Mt) from arable farms with a variety of co-benefits: 3.82 Mt is currently used for fodder and other off-field purposes, whilst 1.45 Mt is chopped and incorporated into soil on the fields for their enrichment. If this chopped and incorporated cereal straw from arable farms were converted into bioethanol, Glithero et al. [6] estimated that it might represent 1.5% of the UK petrol consumption on an energy equivalent basis. However, the variation in regional straw yields across the country – they principally come from East Midlands and East of England - would have a great effect on the indigenous English supply of straw. Notwithstanding these uncertainties, wheat straw offers the potential to significant quantity of sustainable SGB feedstock in the form of bioethanol. In a related farm business or market study of the same cohort of farmers, Glithero et al. [7] discovered that around two-thirds of farmers would supply wheat straw for biofuel use, with the most popular contract length and continuous length of straw supply was either one or three years. They found that arable farmers in England would be willing to sell 2.52 Mt of cereal straw for biofuel use nationally, including 1.65 Mt in the main cereal growing areas of Eastern England. Thus, cereal straw could be diverted from on-farm uses and from straw currently incorporated into the soil. But Glithero et al. [7] suggested that policy interventions might be required to incentivize farmers to engage in this SGB market, and they argued that food and fuel policies must increasingly be integrated to meet societal goals.

1.3. The issues considered

The aim of the present study was to examine the thermodynamic implications of different bioethanol production routes from wheat straw; the cellulosic by-product, or 'waste' stream, from wheat crops. Thermodynamic (energy and exergy) analysis gives rise to differing insights into the relative performance of various process chains. The thermodynamic property known as 'exergy', for example, reflects the ability of undertake 'useful work', but does not represent well heating processes within an energy sector [8]. Thus, energy analysis of four different production paths has first been utilised to evaluate the impact of mechanical work, temperature changes and separating techniques. The *Net Energy Value* (NEV) of each production path or route was then analysed, including the effect of system boundary expansion. Exergetic efficiencies were obtained through chemical and physical exergy calculations, along with some of the electrical inputs to the different processes. Finally, the associated exergetic 'improvement potentials' of the process stages were then determined using the exergetic efficiencies and irreversibility values respectively. These estimates will enable industrialists and policy makers to take account of some of the consequences of alternative bioethanol production routes.

Four different bioethanol production paths have been analysed on a comparative basis. These were (i) the IBUS process [9], which involves the hydrolysis of wheat straw matter with baker's yeast being added to the vessel for monomeric sugar conversion; (ii) the Maas process [10], that uses mechanically reduced straw in a lime pre-treatment vessel containing a solution of lime, water and straw suspended in a continuous mixing vessel; (iii) the Thomsen process [11], that starts with chopped straw being moved into a soaking vessel; and (iv) the TMO process {developed by the since liquidated *TMO Renewables* (Dr. Nigel Francis, *TMO Renewables Ltd.*, private communication, 2012)}, that employs a *separate hydrolysis and fermentation* (SHF) configuration.

2. Materials and methods

2.1. Bioethanol processing routes

2.1.1. Pre-treatment techniques

Bioethanol production from cellulosic feedstocks requires three distinct steps: pre-treatment, total enzymatic hydrolysis, and fermentation [12]. This is typically known as *separate hydrolysis and saccharification* (SHF), although a process of *simultaneous saccharification and fermentation* (SSF) is also available. The latter involves hydrolysis and fermentation steps being carried out simultaneously in the same vessel [13]. The pre-treatment step is needed to increase the substrate digestibility, because lignocellulosic biomass is somewhat intractable in terms of enzymatic hydrolysis, due to various structural factors [14]. Indeed, the structure of wheat straw is dependent on multiple harvesting factors (see Appendix A below), but is primarily comprised of cellulose, hemi-cellulose and lignin - the three basic components of crude biomass. According to Talebnia et al. [15] the composition percentages for these components are generally in the ranges 33–40, 20–25 and 15–20 respectively. The overall success of bioethanol production from wheat straw is largely dependent on the ability of the pre-treatment technique to improve the digestibility of polysaccharides, cellulose and hemi-cellulose contained within the structure of the straw. Cellulose is contained in the outer structure of the lignin, and is further compacted into long polymer chains called '*microfibrils*'. These are linked by short chain, hemi-cellulose polymers [15]. Enzymatic hydrolysis of cellulose will rarely exceed 20% without pre-treatment, unless high enzyme concentrations are used [16]. The aim of pre-treatment is therefore to breakdown the lignin structure, and also to disrupt the crystalline structure of *microfibrils* in order to release cellulose and hemi-cellulose polymer chains [16–19]. It should be noted however that carbohydrate degradation can occur during pretreatment, if conditions are too harsh, leading to the formation of inhibitors such