

Preliminary Investigation of Catalytic Conversion of Biomass-derived Butyrates to Bio-LPG Hydrocarbons in Hydrothermal Media

Introduction

According to the UK Liquefied Petroleum Gases Association (UKLPGA), LPG currently provides secure energy to 2 million UK homes, mostly for off-grid heating where alternative decarbonisation solutions are limited [1]. The aim of this proof-of-principle project is to investigate the conversion of biomass-derived butyrates to C3 and C4 hydrocarbon gases (bio-LPG components), as a route to developing a low-carbon pathway to C3 and C4 hydrocarbons as alternatives to petroleum-derived LPG, which has a global market of US\$125 billion [2].

The carboxylate feedstock (butyric acid and 3-hydroxybutyric acid) can be obtained from the well-known and increasingly popular acetone-butanol-ethanol (ABE) fermentation process [3-4]. Hence, the success of this project can inform the modification of the ABE process as a rich and reliable source of butyrates from biomass, and therefore a commercial source of bio-LPG for various uses as shown in Figure 1.

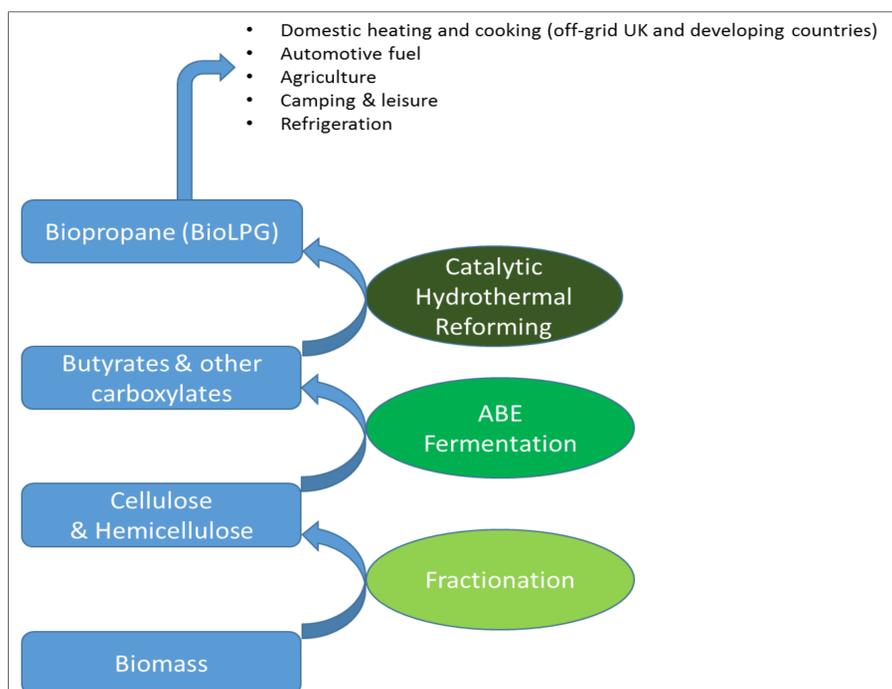


Figure 1: Schematic of proposed process for biopropane production

Rationale

Bio-propane (or bio-LPG) is currently mainly produced as a by-product of catalytic hydroprocessing of vegetable oils and lipids. This process requires the use of large quantities of hydrogen gas, at high volume ratios of up to 650 m³ per m³ of vegetable oil [5]. While a vast amount of the hydrogen gas is recycled and re-used, process costs can be reduced by minimising or eliminating the use of hydrogen. Catalytic decarboxylation is a low-hydrogen reaction that can be used to convert carboxylic acids to alkanes in the presence of catalysts.

State-of-the Art

Since butyrates from modified ABE fermentation are obtained in aqueous solutions, it is therefore sensible to carry out their catalytic conversion in hydrothermal media, thereby saving energy required for feedstock dewatering. Curt et al. [6] applied hydrothermal processing of butyrates to C3 hydrocarbons, achieving butyrate conversion of just about 12%. Although, the authors reported high selectivity towards propane from butyric acid, they also reported the formation of C1 and C2 hydrocarbons, indicating breaking of C-C bonds in the alkyl chain [6]. Other researchers have reported the conversion of waste polyhydroxybutyrate to propene as a recycling method, but the reaction took about 4 h to complete [7].

Research Objectives

The main objectives of this preliminary study are to achieve high feedstock conversions and high product selectivity to bio-LPG component gases at short reaction times. In addition, results from this work will be used to carry out a high-level economic evaluation of bio-LPG production from butyrates on a commercial scale.

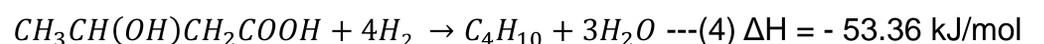
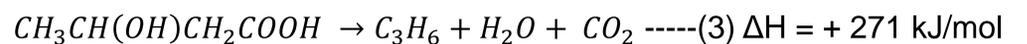
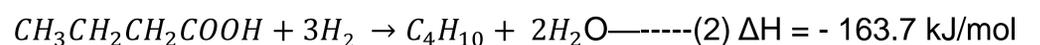
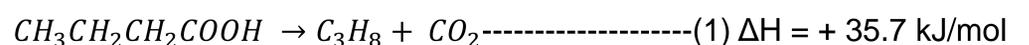


Figure 2. Stirred batch reactor

Materials and Methods

Experiments will be carried out in a hydrothermal stirred batch reactor (Figure 2) in the presence of a selection of commercial and prepared decarboxylation and aqueous-phase reforming catalysts.

The main target reactions during the butyrates conversion include;



Expected Highlights

- High conversions (>90%) of butyrates and selectivities towards C3 and C4 hydrocarbon gases
- Selective catalysts for minimal or no C-C alkyl bond cleavage
- High-level techno-economic assessment of the biomass-to-LPG process via the butyrate route.

References

- [1] UKLPGA, 2019. Gas for off-grid Britain; [2] Grand View Research, 2016. Liquefied Petroleum Gas (LPG) Market Analysis by Source; [3] Sjöblom, M. et al. FEMS Microbiology Letters. 2016, 363 (8), 1-7; [4] Xiao, Z. et al. Biotechnology for Biofuels. 2018, 11, 164-175; [5] Bezergianni S. et al., Fuel. 2012, 638 - 641; [6] Curt R. F. et al. Ind. Eng. Chem. Res. 2011, 50(8), 4420-4424; [7] Li, Y. & Strathmann, T.J., Green Chem., 2019, 21, 5586 - 5597