Semana de Engenharia 2010
Guimarães, 11 a 15 de Outubro

INTENSIFIED BIOPROCESS FOR THE ANAEROBIC CONVERSION OF SYNGAS TO BIOFUELS

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KEYWORDS
Biofuels, syngas, anaerobic microbiology, mass transfer, bioprocessing intensification, bioreactor design, numerical simulation

ABSTRACT

Syngas, composed mainly of CO, H_2 and CO_2 can be produced from several sources, including coal, oil and natural gas, tar sands, recalcitrant wastes and biomass. Syngas can be a potential feedstock for the sustainable production of biofuels and bulk chemicals. The selective biological conversion of syngas is a possible alternative to the chemical route. Nevertheless the biological route remains rather unexplored within the bioprocess engineering community. Some anaerobic micro-organisms have the ability to use CO, H_2 and CO_2 and produce renewable biofuels such as ethanol, butanol, and methane. As in the stage of work planning, this work introduces the main issues in the topic of syngas fermentation to biofuels. The experimental work to be performed aims to develop a new anaerobic bioprocess for the conversion of syngas to biofuels, with principal interest in ethanol, butanol, and CH_4. An oscillatory flow reactor, presenting efficient gas-liquid mass transfer rates, will be explored carrying out proof-of-concept experiments using pure and defined mixed anaerobic cultures. In a later stage, an energy based metabolic model will be developed to predict products formation according to specific environmental conditions.

INTRODUCTION

Biomass-based sources, such as lignocellulosic raw materials and some types of waste, cannot be directly converted to fuels, due to their high complexity and low degradability. Thus, an intermediary process is needed in order to produce intermediate, easier degradable substrates to be ultimately converted to fuels. Gasification is one such early intermediary process, in which carbonaceous material is gasified at high temperature, producing a gas mixture. Synthesis gas, also referred to as syngas, is a product resulting from a gasification process. In gasification, different types of materials can be used, varying from materials, such as coal and char, to organic materials and wastes. The principal components of syngas are carbon monoxide (CO), hydrogen (H_2), and carbon dioxide (CO_2). For efficiently conversion of syngas to biofuels three main issues must be explored: gas-liquid mass transfer; bioreactor design; syngas fermentation, and metabolic modelling. Insights from these aspects are the main topics of the present research.

GAS-LIQUID MASS TRANSFER

Effective syngas utilisation is clearly dependent on gas-liquid mass-transfer rates. Conventional gas-liquid contacting technologies, such as stirred tank reactors, airlift reactors or bubble columns, show low gas-liquid mass transfer rates, also due to the low solubility of the major syngas components in the aqueous culture medium (Bredwell *et al.*, 1999). Volumetric mass-transfer gas-liquid coefficient (k_La) higher than 360 h^{-1} for O_2 is unlikely to be obtained with any of the conventional gas-liquid contacting technologies (Vasconcelos *et al.*, 2003). However, higher k_La (up to 560 h^{-1}) were obtained using a new gas-liquid contacting technology based on oscillatory flow mixing technology featuring a particular combination of flow constrictions and fluid oscillations, which can perform efficiently using minimum power inputs (Reis *et al.*, 2008). Further important features presented by oscillatory flow reactors are linear scale-up, efficient mixing and particle suspension as well as narrow residence time distributions (Mackley and Ni, 1991).

BIOREACTOR DESIGN

Syngas fermentation has been studied using different reactor types, both in batch or continuous operation. The choice of a suitable bioreactor is a matter of matching reaction kinetics with the capabilities of the various bioreactors (Klasson *et al.*, 1991). The reactor properties must be managed in order to allow high mass transfer rates balanced with high cell densities. The stirred tank reactor has been the most applied in syngas fermentation. However, other types of reactor such as, bubble column (Datar *et al.*, 2004) and trickling bed (Cowger *et al.*, 1992) have also been used for the same purpose.

SYNGAS FERMENTATION

Several microorganisms are capable of utilising syngas components to produce valuable products. Combining either mass transfer or reactor design optimisation with microbiology fundamental research is a route of interest in pursue of novel intensified bioprocesses in syngas fermentation. Production of ethanol from syngas has been widely studied since the discovery of Fischer-Tropsch synthesis. Biological syngas conversion to ethanol has gained an increased interest since the isolation of *Clostridium ljungdahlii*, which has the ability to ferment a mixture of CO and H_2 to ethanol and acetic acid. At present, there is significant development in syngas fermentation research and several new species have been discovered and identified that can use syngas components. Several research studies have been carried out in fundamental aspects of syngas fermentation to fuels, especially in process microbiology issues. Syngas fermentation to ethanol by *C. ljungdahlii* is already a commercial process developed by Bioengineering Resources Inc. (BRI energy, 2005). Furthermore, microbiology of syngas bioconversion to biofuels has been recently reviewed (e.g., Sokolova *et al.*, 2009), comprising a wide range of microorganisms from archaea to bacteria, both mesophilic and thermophilic.

METABOLIC MODELLING

Mixed culture fermentation systems can be managed by both engineering and microbiological tools in order to achieve competitive bioprocesses (Rodríguez *et al.*, 2008). A Gibbs-energy-based methodology for mathematical modelling of energy-limited anaerobic ecosystems provides a basis for the description of microbial activities as a function of environmental factors, which will allow enhanced catalysis of specific reactions of interest for process development (Rodríguez *et al.*, 2008). Recently, an approach for predicting the product spectrum as a function of the environmental conditions in anaerobic mixed-culture fermentation processes has been presented (Rodríguez *et al.*, 2006). By considering that energy limitation entail a selective pressure in such ecosystems, product formation reactions which are associated to Gibbs energy yield maximization are favoured by those selective pressures. As a result, microorganisms that are capable of catalysing this optimised set of reactions will be selected by the environment (Rodríguez *et al.*, 2008). This new conceptual model assumes the anaerobic microbial ecosystem as single microorganism. Moreover, such model is described by a simplified metabolic network of the most common fermentative reactions.

PROSPECTIVE WORK

Focused on these issues, a research work has been proposed to explore the possibility of efficiently convert syngas to biofuels of interest (ethanol, butanol, methane), using an optimised reactor and biological cultures to maximise production yield.

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