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# Propagated fixed-bed mixed-acid fermentation: Part I: Effect of volatile solid loading rate and agitation at high pH

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### ABSTRACT

Countercurrent fermentation is a high performing process design for mixed-acid fermentation. However, there are high operating costs associated with moving solids, which is an integral component of this configuration. This study investigated the effect of volatile solid loading rate (VSLR) and agitation in propagated fixed-bed fermentation, a configuration which may be more commercially viable. To evaluate the role of agitation on fixed-bed configuration performance, continuous mixing was compared with periodic mixing. VSLR was also varied and not found to affect acid yields. However, increased VSLR and liquid retention time did result in higher conversions, productivity, acid concentrations, but lower selectivities. Agitation was demonstrated to be important for this fermentor configuration, the periodically-mixed fermentation had the lowest conversion and yields. Operating at a high pH ( $\sim$ 9) contributed to the high selectivity to acetic acid, which might be industrially desirable but at the cost of lower yield compared to a neutral pH.

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#### 1. Introduction

Fossil fuels (e.g., natural gas, petroleum, and coal) currently meet most of the world's energy needs. However, growing demand for these depleting resources (Jefferson, 2006) causes price instability and shortages; and fossil fuel combustion contributes to global warming, acid rain, and pollution (Demirbas, 2007). Sustainable and non-polluting energy sources are becoming increasingly important to meet our growing energy needs and help replace foreign oil with domestic fuels. The carboxylate platform, which converts lignocellulose to liquid fuels, is a promising alternative (Agler et al., 2011).

Lignocellulosic biomass is an important energy source (Carroll and Somerville, 2009). The oldest and most versatile renewable fuel, biomass is most commonly used to produce steam and electricity. As an alternative, using the carboxylate platform, biomass can be converted to liquid transportation fuels and industrial chemicals (Granda and Holtzapple, 2009). Converting biomass into liquid fuel does not cause a net increase in atmospheric carbon dioxide (Ragauskas et al., 2006) because biomass growth removes the same amount of carbon dioxide from the atmosphere that is released during combustion (Sterzinger, 1995). The carboxylate platform has attractive economics and is readily scaled down (Granda et al., 2009; Pham et al., 2010).

The carboxylate platform is being commercialized as the MixAlco™ process, a biomass-to-energy technology that biologi-

cally converts biomass (e.g., lignocellulose, fats, proteins, carbohydrates) into carboxylate salts that are then chemically converted into chemicals and hydrocarbon fuels (Granda and Holtzapple, 2009; Holtzapple et al., 1999). In the fermentation step, biomass is fermented by a mixed-culture of microorganisms to produce carboxylic acids (e.g., acetic acid), which are buffered to form carboxylate salts (e.g., calcium acetate). These salts are precipitated and thermally converted to ketones (e.g., acetone), hydrogenated to mixed alcohols (e.g., isopropanol), and catalytically converted to hydrocarbons (e.g., gasoline, jet fuel). This versatile continuous process uses nearly any biomass feedstock, which minimizes market distortions and food scarcity. It has low capital and operating costs, does not require sterile operating conditions or added enzymes, and has reached the demonstration level of development.

In a countercurrent fermentation, solids and liquids are transported through a series of fermentors (a train) in opposite directions, allowing the least reactive (most digested) biomass to contact the lowest acid concentration, thereby reducing product inhibition. This countercurrent strategy achieves both high product concentration and high conversion (Fu and Holtzapple, 2010). However, at pilot-plant and industrial scales, the high solids content makes filtering and moving biomass difficult and timeconsuming (Domke et al., 2004; Smith, 2011). The equipment used to filter and transport solids is expensive and prone to fouling; however, transporting liquids or slurries is easily accomplished using pumps and piping.

Fixed-bed fermentation, a process in which only the liquid phase is transferred between fermentors in series, provides an



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alternative to the countercurrent configuration. The benefits of a fixed-bed fermentation include minimal solids handling and the potential for high product concentrations and productivities (Agbogbo and Holtzapple, 2007). Both pile fermentation, a configuration in which liquid flows by gravity through a fixed-bed or pile, and a submerged fixed-bed configuration minimize solids handling. However, previous studies demonstrated that fixed-bed fermentation without propagation can result in unsteady product concentrations with time because as the biomass digests, it becomes less reactive and produces less acid (Agbogbo and Holtzapple, 2007).

To address this unsteady-state issue, a propagated fixed-bed fermentation system (Fig. 1) was implemented. In this system, fresh liquid is added to the most-digested fermentor, cascades through four fermentor stages, and exits as product liquid from the least-digested fermentor, while the solid phase remains stationary. The oldest fermentor with the most recalcitrant (digested) biomass is systematically replaced by a fermentor with fresh biomass (Fig. 1). This "round robin" propagation of fermentors allows the system to have fresh substrate and so should achieve quasisteady state and near-constant product concentrations, and still simulate a desirable commercial scenario. Understanding the performance of propagated fixed-bed fermentations helps evaluate the potential benefits of countercurrent flow in carboxylate fermentations, and can guide equipment selection in industrial fermentations.

In certain industrial processes, it is desirable to have high acetic acid concentrations. For example, the market for acetic acid is much larger than the market for higher acids. Additionally, if one is targeting ethylene from ethanol (Granda et al., 2009) or propylene from isopropanol (Pham et al., 2010), it would be desirable to increase selectivity to acetate. One way to accomplish this is by adjusting the fermentation pH. Generally, carboxylate fermentations are conducted at a pH between 5.5 and 6.5, an acceptable pH for acidogens (Khanal, 2008). However, numerous studies have shown that marine microorganisms tolerate alkalinity (Maeda and Taga, 1980). In batch studies, subjecting fermentation bacteria to a pH of >8 has been demonstrated to produce >92% acetic acid (Fu, 2007), compared to 40–60% acetic acid from similar studies at an average pH of 6 (Fu, 2007; Smith, 2011).

In this study, a novel propagated fixed-bed fermentation system was employed to evaluate high pH fermentation under continuous conditions. In addition, the effect of volatile solids loading rate (VSLR) is quantified, and a minimal mixing configuration was used

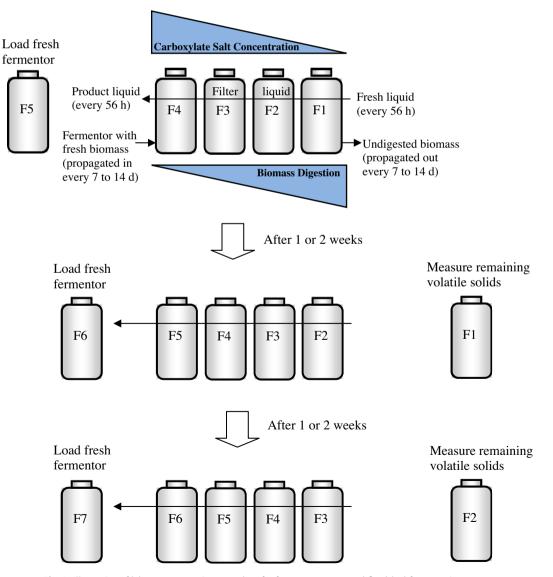


Fig. 1. Illustration of laboratory operating procedure for four-stage propagated fixed-bed fermentation system.

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