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Biodiesel synthesis in an intensified spinning disk reactor

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HIGHLIGHTS

- ▶ We demonstrate an improved design of spinning disk reactor for biodiesel synthesis.
- ▶ The geometric parameters of inter-disk space, and disk topology are shown to have a key effect on performance.
- ▶ The modeling provides new insights into the fluid mechanics of a constrained high shear two phase flow.
- ▶ A quantitative model for conversion as a function of disk speed and geometry is validated.
- ▶ The results raise questions on the extent of mass transfer limitation in biodiesel synthesis.

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ABSTRACT

In this paper we describe an innovation for the intensified synthesis of biodiesel, exploiting a two-disk spinning disk reactor. The reactor comprises two flat disks, located coaxially and parallel to each other with a small gap between the disks. The upper disk is located on a rotating shaft while the lower disk is stationary. The feed liquids are introduced coaxially along the center line of each disk, with mixing commencing in the center of the inter-disk gap. The mixed phases flow radially outwards for ejection and coalescence on the inner containment wall of the reactor. Performance results in the reactor for the continuous synthesis of biodiesel from canola oil and methanol in the presence of a sodium hydroxide catalyst are presented. The effects of disk speed, volumetric flowrate, temperature, disk design, and the gap width between the two disks in the reactor were evaluated. The results show potentially a 20–40-fold decrease in residence time for the attainment of equilibrium compared with that determined for a stirred batch reactor used as a "control". The mathematical modeling of the fluid flow conditions in the reactor is described. This provides further understanding of the potential importance of mixing in determining the reactor performance, pointing to some explanation of the relationship between conversion, flowrate, disk speed and geometry. The inter-disk gap, the reaction temperature, and the surface topology of the disks were the most important factors influencing reactor performance. Surprisingly, reactor performance increased as the inter-disk gap width was reduced. The results of the simulations gave an accurate fit with the experimental reactor performance data using true rate constants which were significantly higher than those reported in the literature. This suggests that some literature data may have not taken full account of mass transfer limitation during experimental determination of rate constants for biodiesel synthesis.

1. Introduction

Spinning disk reactors (SDRs) are one of the process intensification technologies employing high gravity fields. The concept has so far been shown as appropriate for fast and very fast liquid/liquid reactions involving large heat effects, such as polymerizations, synthesis of pharmaceutical products, and fine particle production [1,2]. In a spinning disk reactor, a high gravity field–centrifugal force is created by rotation of a disk surface on which liquid is dispersed as a thin film with the free surface of the liquid in contact with a gas. The gas may either be inert or contain a reactant, and may also act as a cooling or heating medium. Disk speeds can be up to 1000 rpm. Typically the liquid flows radially outward under the centrifugal force in the form of a thin film which may be less than 100 μm thick and so offer a short diffusion path length. The film is unstable and forms waves at the gas–liquid interface. Unsteady film surface waves on the disk surface, coupled with the shearing action of the rotating surface, ensure that micro-mixing and excellent mass and heat transfer are achieved. Extensive mass

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Nomenclature

c_{TG}, c_1, x_1 concentration of tri-glyceride
c_{Met}, c_5, x_5 concentration of methanol
c_{DG}, c_2, x_2 concentration of di-glyceride
c_{Dies}, c_6, x_6 concentration of ester (biodiesel)
c_{MG}, c_3, x_3 concentration of monoglyceride
c_{GL}, c_4, x_4 concentration of glycerol
c_p heat capacity
$\mathbf{D}$ deformation rate (symmetric part of the velocity gradient)
D_{eff} effective diffusivity
DG di-glyceride
Ei activation energy
g acceleration due gravity
GL glycerol
k_1, k_2, k_3, k_4, k_5, k_6, k_i, rate constants (for molar concentrations)
k_1, k_2, k_3, k_4, k_5, k_6, k_i effective rate constants (for molar fractions)
MG monoglyceride
M_B molar mass
p pressure
r_I, r_{II}, r_{III} rate of reaction
r_{x1}, r_{x2}, r_{x3}, r_{x4}, r_{x5}, r_{x6} rates of production for individual components due to reaction
R universal gas constant
t time
T absolute temperature
TG triglyceride
$\mathbf{v}$ velocity vector
V_A nominal molar volume
$V_{mTG\text{-}in}$, $V_{mTG\text{-}out}$ molar rate of triglyceride ester in, and out
$\dot{\gamma} = \sqrt{2\mathbf{D} : \mathbf{D}}$ shear rate
ρ density
μ, μ_B viscosity

and heat transfer studies, and kinetic studies using this technology have shown that residence times, reactant inventories, and impurity levels can be reduced by up to 99% [3–5]. Residence times on the spinning disk range from a few seconds down to fractions of a second, and it is therefore well suited to processes where the inherent reaction kinetics are of the same order or faster than the mixing kinetics. Characteristics of the spinning disk reactor include intense mixing in the thin liquid film, high heat and mass transfer coefficients, short residence times, and plug flow characteristics.

A wide range of applications of SDRs has been explored [4–11]. Significant enhancements in polymerization rates have been obtained within the thin films generated on the rotating reaction surface, compared to classical stirred tank reactors. The distribution of molecular weight properties was also improved. Continuous production of nano- and micro-size particles via reactive crystallization in SDRs has also been reported [6–10]. Spinning disk reactors also have potential for the intensification of both gas–liquid operations [10] and liquid–liquid reactions [11] due to their excellent mass transfer and uniform micro-mixing characteristics. Less work has been reported on liquid–liquid two-phase systems. Short residence time operation on the one hand may improve production efficiency and make continuous processes more viable. On the other hand, if the residence time is too short high conversion yields may not be achievable. In order to attain high reaction rates within a few seconds, high speed, intensive, forced molecular inter-diffusion of the reactant molecules is required. Modified designs of spinning disk reactors which enhance liquid–liquid mass transfer and reaction rate have been described. One type involves two impinging jets which are introduced into rotating and stationary disks through two simple nozzles which are directed toward each other at the center of each disk [12]. This type combines high mixing rate achievable through the impingement process combined with the high shear forces associated with the fluid in contact with the disk surfaces. However, the effect of the impinging jet on the conversion was found to be small at higher rotational speed, especially when the gap between the two disks is very small. Substantial improvements in interfacial mass transfer rate in a range of systems have been demonstrated. This is attributed to higher specific interfacial area, improved internal circulation rates within droplets and due to enhanced rates of interfacial shear on account of increased slip velocity between dispersed and continuous phases.

Here we discuss a novel intensive spinning disk reactor (SDR) developed to explore the possibility of improving the efficiency of biodiesel production. The SDR includes a stationary disk, which is coaxially spaced adjacent to a rotating parallel disk separated by only a fraction of a millimeter. Rather than using a high speed jet, the two immiscible liquid phases are pumped from the centers of the stationary disk and the rotating disk, respectively. The performance of the new spinning disk reactor was studied, quantifying the influence of the separation distance between the disks, the rotational speed, the phase flowrates, reaction temperature, and the topology of the disk surface. A key part of the study was the application of novel finite element software to predict the hydrodynamic behavior of the fluid phases in the inter-disk space, and thus the transport and kinetic behavior. The model reaction system chosen for study was the methyl-esterification of canola oil in the presence of a sodium hydroxide catalyst to form biodiesel and glycerol.

Biodiesel offers an environmentally sound complementary extender for transportation fuels including conventional petroleum diesel and as a partial replacement for gasoline. Improved technology is needed to make biodiesel production from lower grade feedstocks cost-competitive. Biodiesel production involves the esterification of a fat or oil feedstock with methyl alcohol under alkaline conditions in a liquid–liquid environment. It provides a clean burning substitute for petroleum diesel and it is made from naturally produced and renewable feedstocks. These include a wide range of vegetable oils such as sunflower oil, soyabean oil, peanut oil, and rapeseed oil. Another potential source of feedstock is waste tallow and fats derived from meat, fish and chicken processing facilities and from the rendering industry. There is also the potential to produce biodiesel from waste cooking oils which are also a valuable feedstock for potential biodiesel production. Their use as a fuel mitigates pollution potential and the inevitable load which the disposal of these materials places upon waste treatment facilities and on the wider environment. The renewable nature of the feedstock is a major environmental benefit and has the potential to: (a) reduce dependence upon non-renewable fossil fuel (b) assist in the sequestration of carbon dioxide (by photosynthesis of plant based natural oils) from the atmosphere thus partly closing the loop of the carbon cycle (c) utilize waste oils which would otherwise require expensive waste treatment or would be a source of pollution.