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Advantages of Hydrothermal Synthesis to Produce Tunable TiO_2 Nanomicro Sized Photocatalysts and Their Effect in Lignin Degradation
R. Rangel, J. A. Cortés, J. Lara, P. Quintana, J. J. Alvarado-Gil, and O. Contreras
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Advantages of Hydrothermal Synthesis to Produce Tunable TiO_2 Nanomicro Sized Photocatalysts and Their Effect in Lignin Degradation

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Studies on photocatalytic degradation of lignin are scarce, even though it is an effective method for treatment of industrial effluents. In the present work, an advanced oxidation process (AOPs), leading to the photodegradation of lignin aqueous solutions, is proposed by using microstructured (T-MT) and nanostructured (T-NT) titanium dioxide compounds. Hydrothermal synthesis, in accordance with an experimental factorial design considering time of synthesis, NaOH concentration and synthesis temperature, was used to produce tunable TiO_2 photocatalysts for further study of its effects on the degradation of lignin. Photocatalytic reactions were conducted in a micro reactor batch system under UV irradiation. The catalysts were analyzed by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), surface area and porosity analyzer (BET), energy-dispersive X-ray spectroscopy (EDS) and UV-Vis diffuse reflectance spectroscopy. In order to optimize the yield reaction, an experimental factorial design was performed. According to our results, nanostructured TiO_2 consisting in different structural features and light absorption properties were produced using this method. It is shown that T-MT and T-NT compounds exhibit a wide range of values, for the kinetic parameters, in photoinduced degradation of methylene blue (MB) and lignin.

Keywords: Nanostructured titania; titania nanotubes; lignin degradation; hydrothermal; photo catalysis

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Experimental methodology to calculate the local relative light intensity in heterogeneous TiO2/UV-A photocatalytic reactors

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Short Communication

Experimental methodology to calculate the local relative light intensity in heterogeneous TiO_2/UV-A photocatalytic reactors

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ABSTRACT

In the field of heterogeneous photocatalysis, catalyst concentration is one of the main parameters that restricts light availability, specifically in photocatalytic annular slurry reactors design. Therefore, data that describes the dependence of energy on both, distance and catalyst concentration is needed. This paper proposes the local relative light intensity (LRLI) as a quantity that represents the residual energy on radial distance. Experimental measurements of LRLI were made from 0 mm to 25 mm, using two commercial TiO_2 powders in a wide range of concentration (200 to 1000 mg/L). Results show that residual energy was less than 80% at 6 mm from the source, for both catalysts in all concentrations. Furthermore, a forward-scattered behavior was detected, the LRLI profiles (LRLI vs radial distance) followed an exponential decay model. All profiles were correlated as a catalysts concentration function. Information obtained was used to develop a methodology to calculate the LRLI values at any radial distance for a settle catalyst concentration. The calculated values of LRLI approaches real data with a relative local accumulated error less than 10% for both catalysts. This methodology may be applied to calculate the energy available in any TiO_2/UV-A annular slurry system.

1. Introduction

The heterogeneous photocatalysis TiO_2/UV-A is one of the advanced oxidation processes used to remove toxic, recalcitrant and colored pollutants in water. The ultraviolet light (UV-A) has enough energy to induce an excited state in semiconductor (TiO_2) and promotes the creation of electron–hole pairs, this allows the reactive oxygen species production (*e.g.* hydroxyl radicals) (Liao et al., 2013). These compounds are highly reactive with organic pollutants until mineralization is reached (Chong et al., 2010; Akpan and Hameed, 2009; Nakata and Fujishima, 2012). The light dependence of photocatalytic process has led to several reactor configurations and the efficiency varies from one system to another (McCullagh et al., 2011). The annular slurry photoreactor is widely used (Moreira et al., 2011; Yang et al., 2005; Zekri and Colbeau-Justin, 2013; Ballari et al., 2008; Imoberdorf et al., 2008), it is considered the most efficient configuration because it takes advantage of emitted radiation, increasing process effectiveness (De Lasa et al., 2005). Nevertheless, the efficiency of this kind of configuration is restricted by energy available along suspended media. Some efficiency definitions (*e.g.* photonic efficiency),

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ORIGINAL PAPER

Reduction of greenhouse gas emissions from steam power plants through optimal integration with algae and cogeneration systems

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Abstract This paper presents an optimization approach for mitigating CO_2 emissions in the electric power generation through integrated algae and cogeneration systems. A framework is proposed for the integration of biofixation of CO_2 through the cultivation of microalgae, conversion of microalgae to biodiesel, and a steam power plant with cogeneration that is thermally coupled with an industrial facility. A systematic multi-objective optimization approach is developed to integrate the considered units while simultaneously addressing technical, economic, and environmental objectives. The solution of the optimization problem is carried out via a hierarchical decomposition approach, a genetic algorithm, and the ε-constraint method for solving the multi-objective optimization problem. A case study is considered to integrate an existing thermoelectric power station in Mexico with an algae-and-cogeneration system. The results show that important environmental, economic, and energy benefits can be achieved as a result of the proposed integration approach.

Keywords Combined heat and power (cogeneration) · GHG mitigation · Biological capture of CO_2 · Microalgae biodiesel production · Steam power plants · Sustainable energy systems

List of symbols

Parameters

C_{BD}	Unit price for biodiesel produced (\$/ton)
C_{bf}	Unit cost for biofuel bf (\$/ton)
C_{bm}	Unit cost for external biomass bm (\$/ton)
$C_{\mathrm{ABS}}^{\mathrm{CENT}}$	Concentration of algal biomass (g/L)
C_{EP}	Unit price for electricity (\$/MW)
C_{f}	Unit cost for fossil fuel f (\$/ton)
C_{GLY}	Unit price for glycerol produced (\$/ton)
C_{hex}	Unit cost for hexane (\$/ton)
C_{n}	Unit cost for nutrient n (\$/ton)
C_{w}	Unit cost for make-up water (\$/ton)
H_{Y}	Hours of operation for the plant (h)
H_{V}	Heating value (MJ/ton)
K_{F}	Factor used to annualize the capital costs
Ghge	Unit greenhouse gas emissions (ton CO_2 equiv./MJ)
S^{GHG}	Unit subsidy for reduction of GHG emissions (\$/ton)
w_{OIL}	Lipid content in algal biomass (wt% of dry biomass)
ε	Parameter of the ε-constraint method
$\alpha_{\mathrm{AC}}^{\mathrm{CO_2}}$	Utilization efficiency of CO_2
$\alpha_{\mathrm{AH}}^{\mathrm{CENT}}$	Recovery fraction of algal biomass in secondary harvesting (centrifugation)
$\alpha_{\mathrm{AH}}^{\mathrm{FLOC}}$	Recovery fraction of algal biomass in primary harvesting (flocculation)

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Synthesis of Eco-Industrial Parks Interacting with a Surrounding Watershed

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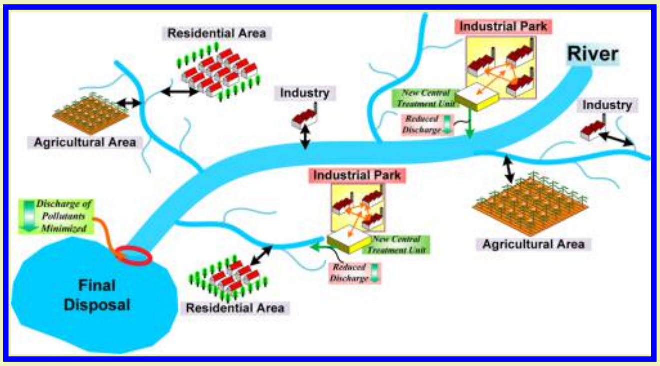

ABSTRACT: Industrial facilities impacting a watershed may be clustered into groups based on their geographical locations. Water usage and discharge for each clustered group of industries may be integrated through the introduction of an eco-industrial park (EIP). This paper presents a mathematical programming model for water integration of EIPs to be synthesized with the purpose of mitigating the environmental impact of industrial effluents discharged into watersheds. The model considers the creation of multiple EIPs, their location, sizing, and tasks. To determine the effect of the discharges on the surrounding watershed, a material flow analysis (MFA) model was coupled with water recycle strategies within the industrial facilities and the associated EIPs. The MFA characterizes the interaction of individual discharges and tracks the impact of the natural (physical, chemical, and biological) phenomena within the watershed on the fate and transport of pollutants. A multiobjective optimization formulation is developed to guide the decisions for multiplant water integration while accounting for the impact on the watershed. The objective function reconciles the minimization of the environmental impact on the watershed, the minimization of the total annualized cost of the water-management system, which includes the cost of fresh water, effluent treatment, and piping and pumping associated with the eco-industrial parks. An example is presented to show the scope and capabilities of the proposed optimization approach.

KEYWORDS: *Eco-industrial parks, Material flow analysis, Water integration, Recycle and reuse networks, Sustainable watersheds*

■ INTRODUCTION

Substantial amounts of water are used in and discharged from industrial facilities. The discharged effluents are typically laden with various pollutants and may lead to major impact on the surrounding watersheds. An effective strategy in reducing water usage and discharge for industrial facilities is to synthesize recycle and reuse water networks for mass integration within the industrial facilities.[1−3] The synthesis of water networks has been extended from intraplant integration to interplant integration through the use of the concept of eco-industrial parks (EIP). In general, the EIP involves industrial symbiosis to integrate various forms of materials and energy as part of the emerging field of industrial ecology.[4−7] In the case of water integration within an EIP, adjacent industries can exchange their resources (in this case water streams) and common infrastructure (e.g., treatment units) to reduce the consumption of fresh resources and the discharge of effluents to the environment.[8−11] Figure 1 shows schematically an EIP composed of several industrial plants where it is possible to recycle wastewater streams to the same plant or to other plants. Additionally, a central treatment facility may be used to receive and treat wastewater streams to enable recycle to the participating plants. Consequently, water integration is improved in the interplant integration compared to the single-plant integration. This integration reduces the overall

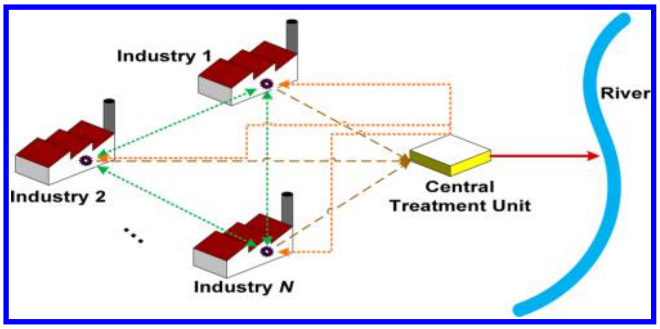

Figure 1. General configuration for an eco-industrial park.

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Correlations for the prediction of the density and viscosity of 1-alcohols at high pressures

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ABSTRACT

We present a correlation for the 1-alcohols density at high pressure based upon the Tait equation. The new equation includes a generalized correlation for the calculation of the density of 1-alcohols at atmospheric pressure and correlates the density of methanol to 1-decanol from (173.15 to 373.15) K at pressures up to 279 MPa within an average absolute percentage deviation of 0.11% from the experimental density values. Also, we use this equation to obtain a model to correlate the liquid viscosities of 1-alcohols. The new model correlates the viscosity at atmospheric pressure within an average absolute percentage deviation of 2.14% from the experimental values. At high pressures (up to 423 MPa), the new model correlates the viscosity of 1-alcohols (methanol through 1-hexadecanol) at temperatures from (293 to 423) K within an average absolute percentage deviation of 3.38%.

1. Introduction

Generalized correlations for the prediction of thermodynamic properties such as density and viscosity at high pressures are important for the design of unit operations equipment [1]. However, it is not always possible to find experimental data in the literature for the thermodynamic properties of interest, consequently many researchers have developed models to predict the properties of different homologous series [2,3].

Assael et al. [4] develop a correlation as a function of the reduced temperature and the number of atom carbons for the prediction of 1-alcohol densities at high pressures. Their correlation is valid for 1-alcohols from ethanol to 1-decanol at pressures up to 100 MPa and from (278 to 374) K.

For the prediction of the viscosities of 1-alcohols, Teja et al. [5] developed a generalized model using the corresponding states principle (GCSP). This model can be used to predict the viscosity of pure components and binary mixtures of liquids. They applied this correlation to 1-alcohols successfully. Nhaesi et al. [6] used the three-body McAllister equation to predict the kinematic viscosity of multicomponent mixtures of *n*-alkanes at atmospheric pressure. Later, Shan et al. [7] showed that this equation can be used to predict the kinematic viscosity of multicomponent mixtures of 1-alcohols within an average percentage deviation of 1.20% from the experimental viscosity measurements. This model requires the kinematic viscosity of the pure components of the mixture at each temperature.

Sun and Teja [8] extended the model based upon rough hard sphere (RHS) theory for the calculation of the viscosity of many components including 1-alkanols. The rough-hard-sphere concept was originally proposed by Chandler [9] and extended by Assael et al. [4]. They expressed the reduced viscosity in terms of the reduced molar volume and parameters that account for deviations of the transport properties of the fluid from those of smooth hard spheres. Xuan et al. [10] used the Tait equation to predict the viscosities of n-alkanes, aromatics and 1-alcohols at high pressures. Unfortunately, their equation is not a generalized correlation since it requires of two characteristic parameters for each fluid at each temperature.

In this work, we propose a generalized correlation for the prediction of the density and viscosity at high pressures for 1-alcohols. For the density, the new correlation is based upon the Tait equation and for the viscosity we propose a simple relationship between the viscosity and the density. The new correlations use the temperature and the number of carbon atoms as variables.

2. Methodology

2.1. Compressed liquid density

Previously, Assael et al. [4] reported a successful equation for the correlation of the density of 1-alcohols. They used the Tait

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Density and Viscosity of Binary Liquid Mixtures of Ethanol + 1-Hexanol and Ethanol + 1-Heptanol from (293.15 to 328.15) K at 0.1 MPa

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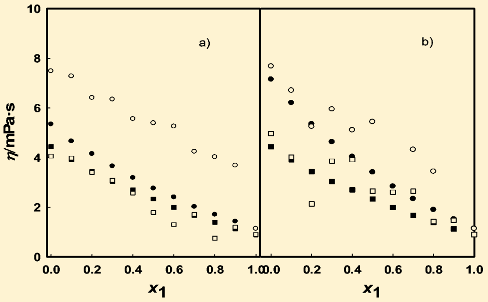

ABSTRACT: This paper presents experimental viscosity and density measurements for two binary mixtures of ethanol with 1-hexanol and 1-heptanol that cover the complete composition range from (293.15 to 328.15) K at 0.1 MPa. A vibrating tube densimeter provides density measurements, whereas viscosities come from a pellet microviscometer. The excess molar volumes calculated from the experimental data have positive deviations from ideality over the temperature range. Calculated viscosity deviations from the experimental data show negative deviations from a mole fraction weighted average of the pure component viscosities over the temperature range. A Redlich–Kister type equation correlates the data satisfactorily. We have correlated the three-body McAllister to the experimental kinematic viscosity. Comparison of the experimental viscosity data to predictions from a generalized, three-body McAllister and a generalized corresponding states principle (GCSP) equation shows that the generalized McAllister equation is superior predicting the kinematic viscosity within an average absolute percentage deviation of 1.24%. Finally, molecular dynamics was performed to compare density and viscosity results with those obtained experimentally. Results for density agree with the experimental measurements, whereas viscosity calculations are beyond the experimental error.

1. INTRODUCTION

The viscosities for liquid binary mixtures of alcohols are important in chemical engineering applications, such as flow in pipes, in heat and mass transfer operations, and in the design of cryogenic systems. The need for a database of accurate properties such as densities and viscosities is essential to develop predictive models. Mixtures of ethanol + 1-hexanol or + 1-heptanol are used as solvents in liquid–liquid extraction therefore thermodynamic properties of these systems are needed. Recently, Rahamn et al.[1] have shown that ethanol extraction from aqueous solutions can be done with 1-hexanol as solvent. This will replace common solvents such as ethers, acetates, or ketones. In addition, these mixtures have been used as additives to gasolines. 1-Hexanol allows more ethanol in the diesel blend,[2] improving blend tolerance for water and keeping the blend fuel stable with time. Thermodynamic properties of 1-alcohols in the liquid phase are strongly influence by the influence of hydrogen bonding; however, the conformation of small alcohol molecules[3] in the thermodynamic properties has been studied in pure alcohol mixtures, but it has not done with 1-alcohols mixtures with a large chain.

In recent years, an effort has evolved to develop predictive models for viscosities, and several models are available in the literature. Rauf[4] et al. report equations for the dynamic viscosity of ethanol + 1-heptanol from (288.15 to 323.15) K. Unfortunately, they did not report their experimental values. Few authors have measured the densities and viscosities of the mixtures considered in this work. Faria et al.[5] used a vibrating tube densimeter and a Canon-Fenske viscosimeter to measure the density and viscosity of the ethanol + 1-heptanol at (283.15 to 313.15) K. Ali et al.[6] measured the densities and viscosities of ethanol + 1-hexanol at 303.15 K. They used a Pyrex glass pycnometer and a Cannon-Ubbelhode viscosimeter to measure the densities and viscosities of this mixture.

An alternative method to know the density and viscosity of a mixture is to use molecular dynamics simulation with an adequate description of the potential energy of the system. Previously, we have shown that density calculations[7] agree with the experimental density measurements for hydrocarbon mixtures. Molecular dynamic calculations have been performed for ethanol,[8−12] 1-hexanol,[8,13,14] and 1-heptanol.[8,13] Molecular dynamics simulation of liquid density for pure alcohols from (288 to 338) K have been performed by Kulschewski and Pleiss.[15] They found out that their density calculations agree with the experimental measurements within an average absolute percentage deviation of less than 0.6% for ethanol, 1-hexanol, and

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Chemical Engineering Thermodynamics

Densities and viscosities of binary mixtures of *n*-decane + 1-pentanol, + 1-hexanol, + 1-heptanol at temperatures from 293.15 to 363.15 K and atmospheric pressure[☆]

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ABSTRACT

Densities (ρ) and dynamic viscosities (η) for three binary mixtures of *n*-decane with 1-pentanol, 1-hexanol and 1-heptanol are presented at temperatures from 293.15 to 363.15 K and atmospheric pressure over the entire composition range. The density and viscosity are measured using a vibrating tube densimeter and a cylindrical Couette type rotating viscometer, respectively. Excess molar volumes (V^E), viscosity deviations ($\Delta\eta$) and excess Gibbs energy of activation of viscous flow (ΔG^{*E}) are calculated from the experimental measurements. Intermolecular and structural interactions are indicated by the sign and magnitude of these properties. Partial molar volumes and infinity dilution molar partial volumes are also calculated for each binary system. These results are correlated using Redlich–Kister type equations.

1. Introduction

A complete knowledge of thermodynamic and transport properties of liquid mixtures is essential for numerous industrial processes, in particular for chemical engineering industries. These properties are necessary in the modeling, design, construction, and optimization of process equipment such as condensers, heat transfer equipment, and distillation columns.

There has been a systematic study of the excess thermodynamic and transport properties for 1-alcohol + *n*-alkane mixtures. These properties have been extensively analyzed from both of experimental and theoretical points of view. From the experimental point of view, the analysis is important because it provides information about composition related changes, hydrogen bonding, and effects of size and structure of the molecules. This information allows the understanding of the molecular structure and the ruling intermolecular interactions. This knowledge can be used to develop models and theories about the mixtures behavior. In the last years there have been several efforts to develop models for excess properties such as enthalpy [1–6] and heat capacity [2,7–10]. Also, it is worth to mention the association models [1,4,11–13] and the group contribution methods [14–17] for the molar volume.

For 1-alcohol + *n*-alkane there are numerous reports on experimental data for excess molar volume or density [18–30] and viscosity [31–39]. Different thermodynamic properties for the binary mixtures with *n*-decane and 1-pentanol, 1-hexanol, or 1-heptanol have been reported in the literature. These properties are the excess enthalpy [40] and the heat capacity [41]. Density and excess volume data have been reported by different authors. The excess volumes for *n*-decane + 1-pentanol have been reported by Yun *et al.* [42], Al-Dujaili and Awwad [28] and Kaur *et al.* [43] at 298.15 K. Densities at other temperatures are measured by Al-Dujaili and Awwad [28] at 288.15, 308.15 and 318.15 K. Experimental densities for the mixture of *n*-decane + 1-hexanol are measured at 298.15 K by Treszczanowicz and Benson [24], Kaur *et al.* [43] and Dubey and Sharma [26]. Dubey and Sharma [26] reported densities for this mixture at 303.15 and 308.15 K. To the best of our knowledge, density measurements for the binary *n*-decane + 1-heptanol do not exist in the literature.

In recent years there has been an increasing interest on the viscosities of liquid mixtures. For example, the study of the viscosity of *n*-alkane + 1-alcohol mixtures, together with other thermodynamic properties, will allow us to know the molecular interactions and structure of these liquid mixtures. Some of these systems exhibit a peculiar behavior [31,34,44–46] which cannot be explained in terms of traditional approaches that have been observed experimentally. Experimental viscosities have been only measured for the mixture *n*-decane + 1-hexanol at 298.15, 303.15, and 308.15 K [26].

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