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**Predicting the Adsorption of Second Generation Biofuels by Polymeric Resins with
Applications for *In Situ* Product Recovery (ISPR)**

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Abstract

The application of hydrophobic polymeric resins as solid-phase adsorbent materials for the recovery and purification of prospective second generation biofuel compounds, including ethanol, iso-propanol, n-propanol, iso-butanol, n-butanol, 2-methyl-1-butanol, 3-methyl-1-butanol, and n-pentanol, has been investigated. A simple, yet robust correlation has been proposed to model the relative equilibrium partitioning behavior of a series of branched and n-alcohols as a function of their relative hydrophobicity, and has been applied to ultimately predict their adsorption potential. The proposed model adequately predicts the adsorption behavior of the entire series of alcohols studied, as well as with six different adsorbent phases composed of three different polymer matrices. Those resins with a non-polar monomeric structure and high specific surface area provided the highest overall adsorption of each of the studied compounds. Meanwhile, longer chain alcohols were subject to greater adsorption due to their increasingly hydrophobic nature. Among the tested series of alcohols, five-carbon isomers displayed the greatest potential for economical recovery in future, multiphase bioprocess designs. The present study provides the first demonstration of the ability of hydrophobic polymer resins to serve as effective *in situ* product recovery (ISPR) devices for the production of second generation biofuels.

Keywords: biofuels; *in situ* product recovery; adsorption.

Introduction

While efficient fermentation pathways exist for the synthesis of alcohol biofuels from renewable resources, biocatalyst productivity becomes limited by inhibitory concentrations of these products at relatively low titers (Bowles and Ellefson, 1985; Ingram, 1990; Jones and Woods, 1986). Such effects of feedback inhibition can be circumvented through integrated bioreactor designs employing *in situ* product recovery (ISPR) (Schugerl, 2000). Polymer resin materials have attracted attention in recent years as auxiliary phases in ISPR designs (Prpich and Daugulis, 2007; Qureshi et al., 2005; Zhou and Cho, 2003). In addition, we have explored the prospects of polymeric resins for ISPR in n-butanol fermentations with *Clostridium acetobutylicum* (Nielsen and Prather, 2009). The adsorption mechanism of n-alcohols occurs at resin surfaces via hydrophobic interactions (i.e., Van der Waals forces) existing between the polymer matrix and the alkyl chain of the alcohol (Carey and Sundberg, 2000). Incorporation of nonpolar monomer units and side chains (such as aromatic groups, for example) enhances the hydrophobic nature of adsorbent materials (Zhou and Cho, 2003). Accordingly, poly(styrene-*co*-divinylbenzene) sorbents materials routinely demonstrate the greatest adsorption affinity for n-alcohols. With this polymer matrix, solute molecules strongly associate with the π - π bonds within the phenyl side chain (Fontanals et al., 2005). Total interactions are enhanced by materials with high specific surface area, providing greater accessibility to those hydrophobic sites. This behavior is supported by the data in Table 1 which compares the experimental resin-aqueous n-butanol equilibrium partitioning coefficients of various poly(styrene-*co*-divinylbenzene) resins as a function of their respective specific surface areas.

The relative hydrophilic or hydrophobic nature of a solute, A , can be characterized by the octanol-water partitioning coefficient, $K_{O/W}$:

$$K_{O/W,A} = \frac{[A]_{octanol}}{[A]_{water}} \quad (1)$$

This empirical, equilibrium relationship quantifies the manner by which A distributes between water and n-octanol phases, and is typically represented as the logarithm of that value ($\text{Log}K_{O/W,A}$). More hydrophobic compounds have higher $K_{O/W,A}$ values because they preferentially accumulate in the n-octanol phase. In an analogous manner, the adsorption potential of a particular resin (r_i) for the same solute by measuring the equilibrium resin-water partitioning coefficient, $K_{R/W,A,r_i}$, can be quantified as:

$$K_{R/W,A,r_i} = \frac{L_{A,r_i}}{[A]_{aq}} \quad (2)$$

where L_{A,r_i} is the specific loading of A on resin r_i at equilibrium. Since the mechanism of adsorption is driven by hydrophobic interactions between the solute molecules and the resin surface, the greatest overall adsorption will occur on the most hydrophobic resins, as well as by those resins with high specific surface areas. Likewise, the more highly hydrophobic solutes should experience the strongest interactions with the resin phase and thus be subject to the greatest adsorption. Accordingly, we hypothesized that the adsorption of another prospective solute (B) on resin r_i could be directly predicted if 1) the adsorption characteristics (i.e., equilibrium isotherm) of solute A onto resin r_i are well characterized, and 2) the relative hydrophobicities of A and B can be directly compared. With such information, we propose that the equilibrium partitioning of B between an aqueous solution and resin r_i can be predicted as:

$$K_{R/W,B,x_i} = K_{R/W,A,x_i} \frac{K_{O/W,B}}{K_{O/W,A}} \quad (3)$$

If found to be valid, Equation 3 would represent a useful correlation to assess the suitability of previously characterized resins for prospective applications. Thus, the procedure by which suitable resins can be identified for the adsorption of a desired solute will be expedited, allowing novel process designs to be rapidly configured without extensive material screening.

Recently, *Escherichia coli* has been engineered to produce a variety of n- and branched chain alcohols, including n-propanol, iso-butanol, n-butanol, 2-methyl-1-butanol, 3-methyl-1-butanol, and n-pentanol, (Atsumi et al., 2008). The hydrophobicity of these and other alcohols of microbial relevance are compared in Table 2. It has been postulated that several of these compounds could serve as superior alternatives to conventional liquid biofuels (i.e., ethanol and n-butanol). Subsequent investigations have further explored the metabolic engineering of *E. coli* for enhanced production of 2-methyl-1-butanol (Cann and Liao, 2008) and 3-methyl-1-butanol (Connor and Liao, 2008). Meanwhile, Gevo, Inc. (USA) is presently exploring the development of large-scale iso-butanol fermentations (Ritter, 2008). However, despite their favorable thermodynamic properties, it has been demonstrated that the cytotoxicity of alcohols increases with the carbon chain length (Heipieper and Debont, 1994; Osborne et al., 1990; Vermue et al., 1993). For instance, our preliminary experiments indicate that growing cultures of *E. coli* become inhibited by as little as 3 g/L n-pentanol (unpublished data). Thus, it is with second generation biofuel producing microorganisms that the use of ISPR designs may be most beneficial to promote efficient product recovery and reduce

product inhibition. Here we explore the utility of polymer resin materials for the ISPR of such prospective second generation biofuels by characterizing their ability to adsorb such compounds from aqueous solutions and fermentation-relevant conditions. In so doing, we have developed a simple, yet novel correlation by which the adsorption of prospective solutes by previously characterized resins can be quickly and easily predicted.

Methods

Chemicals. All chemicals were obtained from Sigma-Aldrich (St. Louis, MO).

Resins. Dupont Hytrel® 8206 was generously provided by Dupont (Wilmington, DE). Dowex® Optipore L-493 and SD-2, Dowex® M43, Diaion® HP-20 and HP-2MG were purchased from Sigma-Aldrich (St. Louis, MO). Relevant physical properties of these polymer resins are listed in Table 3 (where available). To allow for appropriate comparison, all calculations were based on dry resin weight. All resins were dried at 37°C for 72 h to remove excess moisture prior to use. Resins were otherwise used as received from their respective suppliers with no other pre-treatment.

Analytical methods. Aqueous alcohol concentrations were measured both before and after equilibration with resins via HPLC (1100 series, Agilent, Santa Clara, CA). Separation was achieved on a ZORBAX Eclipse XDB-C18 column (Agilent, Santa Clara, CA). The column was operated at a temperature of 50°C. High purity water was used as the mobile phase at a flow rate of 3.5 mL/min. Analytes were detected using a refractive index detector. External standards were prepared to provide calibration. Literature values of

Log $K_{O/W}$ values were obtained from the on-line software package ALOGPS 2.1 (Tetko et al., 2005), and are listed in Table 2.

Adsorption experiments. Equilibrium adsorption experiments were performed in sterile 25 mL glass vials containing 10 mL aqueous solution and 0.5 to 1 g of resin. Solutions were prepared in sterile deionized water (pH 7) with an individual solute (ethanol, isopropanol, n-propanol, iso-butanol, n-butanol, 2-methyl-1-butanol, and 3-methyl-1-butanol, or n-pentanol) at initial concentrations ranging between 67.5 and 675 mM (equivalent to 0.5-5% (wt./vol.) for n-butanol). Mixtures were equilibrated for 24 h at 37°C, with agitation at 250 rpm (Preliminary experiments have indicated that greater than 65% of adsorption occurs within 30 minutes, and more than 95% after 3 hours; data not shown). A temperature of 37°C was selected due to its relevance with respect to the culture of many biofuel fermenting microbes. After measuring solute concentrations both before and after equilibration with a particular fraction of resin r_i (X_{r_i}), the specific loading (L_{B,r_i}) and partitioning coefficient ($K_{R/W,B,r_i}$) of a prospective solute (B) could be determined by the following relationships:

$$X_{r_i} = \frac{m_{r_i}}{V_{Aq}} \quad (4)$$

$$L_{B,r_i} = \frac{([B]_{aq} - [B]_{aq,0})}{X_{r_i}} \quad (5)$$

$$K_{R/W,B,r_i} = \frac{L_{B,r_i}}{[B]_{aq}} \quad (6)$$

where $[B]_{aq}$ represents the concentration of solute B in the aqueous phase, V_{Aq} is the volume of aqueous solution, m_{ri} is the mass of resin r_i , and t_0 and t_{eq} represent time at initial (immediately prior to mixing resins and alcohol solutions) and equilibrium (after 24 hours) conditions, respectively. Experiments were performed in triplicate to provide an assessment of experimental error.

Modeling biofuel adsorption. Adsorption equilibrium data, measured as a function of equilibrated aqueous n-butanol concentration, were fit to both Langmuir and Freundlich isotherms, given by Equations 7 and 8, respectively:

$$L_{B,r_i} = \frac{L_{B,r_i,max} \cdot b_{B,r_i} \cdot [B]_{aq}}{1 + b_{B,r_i} \cdot [B]_{aq}} \quad (7)$$

$$L_{B,r_i} = K_{F,B,r_i} \cdot [B]_{aq}^{\left(\frac{1}{n_{B,r_i}}\right)} \quad (8)$$

Where, for the adsorption of compound B on resin r_i , $L_{B,r_i,max}$ represents the maximum (or, saturated) specific loading, b_{B,r_i} represents the Langmuir adsorption constant, K_{F,B,r_i} represents the Freundlich adsorption constant, and n_{B,r_i} the Freundlich exponent.

Parameter estimates were obtained via nonlinear least-squares regression on Equations 7 and 8 using the intrinsic MATLAB® function *nlinfit*. All error associated with parameter estimates are reported at one standard deviation. By definition (Equation 2), the equilibrium resin-aqueous partitioning coefficient can also be derived as a function of $[B]_{aq}$ for above respective models as:

$$K_{R/W,B,r_i} = \frac{L_{B,r_i,max} \cdot b_{B,r_i}}{1 + b_{B,r_i} \cdot [B]_{aq}} \quad (9)$$

$$K_{R/W, B, r_i} = K_{F, B, r_i} \cdot [B]_{aq}^{\left(\frac{1}{n_{B, r_i}} - 1\right)} \quad (10)$$

All predictions made in this study were performed using n-butanol as a reference solute (thus, A corresponds to n-butanol in the terminology used throughout). Aqueous n-butanol concentrations in equilibrium with an adsorbent resin phase can be predicted for any specific set of initial conditions by solving for the value of $[A]_{aq}$ which satisfies the root of the following material balance equation:

$$0 = ([A]_{aq,0} - [A]_{aq}) \cdot V_{aq} - L_{A, r_i} \cdot X_{r_i} \cdot V_{aq} \quad (11)$$

By application of the proposed model (Equation 3), the adsorption behavior of a potential target solute (B) from a solution initially containing an equimolar concentration of that compound could then be predicted.

Results

Dowex® Optipore L-493 and SD-2, Dowex® M43, and Diaion® HP-20 are each poly(styrene-*co*-divinylbenzene) -derived resins that were previously identified as highly n-butanol adsorbent (Nielsen and Prather, 2008). Diaion® HP-2MG is a poly(methacrylate) -based resin, whereas Hytrel® 8206 is a polyester of poly(butylene phthalate). These two materials showed lower n-butanol adsorption potentials. The n-butanol adsorption equilibria for each resin was fit via linear least-squares regression to both Langmuir (Equation 7) and Freundlich (Equation 8) isotherms. In all cases, Freundlich isotherms best represented the experimental data, as evidenced through both qualitative inspections and minimization of the standard errors of estimation (results not shown). These results, together with the best-fit parameter estimates, are provided in

Figure 1. Also presented in Figure 1 are the Gibb's free energies associated with n-butanol adsorption by each of the studied resins under the conditions examined, as estimated by the following relationship (Huang et al., 2007):

$$\Delta G_{A, r_i} = -R \cdot T \cdot n_{A, r_i} \quad (12)$$

The adsorption potential of a series of both branched and n-alcohol biofuels was then subsequently investigated for each of the studied resins. For any known initial concentration, the aqueous-resin equilibrium partitioning coefficient between resin r_i and prospective solute B can be predicted according to Equation 3, using an estimate of $K_{R/W, A, r_i}$ that corresponds to an equimolar initial concentration of n-butanol (A) as a reference solute. For example, consider the adsorption of n-butanol from a solution that initially contained 67.5 mM n-butanol by Dowex® Optipore L-493 with a resin fraction of 0.04 kg L⁻¹. Then, by combining the resin-specific equilibrium isotherm with Equation 9 it would be predicted that the equilibrated n-butanol concentration in the aqueous phase would be 13.5 mM, while the resin-aqueous equilibrium partitioning coefficient would be predicted to be 103 mmol kg⁻¹ mM⁻¹. According to Equation 3, we could then predict that from a solution containing 67.5 mM of 2-methyl-1-butanol or n-pentanol, for example, 0.04 kg L⁻¹ of Dowex® Optipore L-493 would accordingly achieve equilibrium partitioning coefficients of 270 and 352 mmol kg⁻¹ mM⁻¹, respectively. These predicted values agree well with their respective experimental measurements of 254 and 355 mmol kg⁻¹ mM⁻¹. In fact, as seen in Figure 2, the experimental and predicted equilibrium partitioning coefficients for all of the resins studied and each target alcohol were in good agreement, as indicated by strong correlations with $y = x$. The strength of the observed correlations confirm the validity of the relationship proposed in Equation 3, while also

suggesting that the presented model is equivalently compatible for use with resins of different chemical structures. These findings also further demonstrate that the adsorption mechanism of these prospective biofuel compounds occurs via hydrophobic interactions with the resin phase.

As was previously observed for n-butanol (Nielsen and Prather, 2008), Dowex® Optipore L-493 was also found to provide the greatest overall adsorption for all other alcohols of the tested series. Accordingly, the remainder of our study focused on the use of Dowex® Optipore L-493 as a model resin phase. To better understand the adsorption equilibria of each solute with this material, the equilibrium isotherms for the alcohol series were first determined, and are plotted in Figure 3. From these data it is clear that as the alkyl chain length of the solute is increased, so too is its relative adsorption potential as a direct result of its increasingly hydrophobic nature. No differences were noted between the branched chain isomers 2-methyl-1-butanol and 3-methyl-1-butanol, two solutes with identical values of $LogK_{OW}$ (Table 2). Also provided in the Figure 3 (see inset) are the best-fit estimates associated with Freundlich isotherm parameters for each solute. As above, the Gibb's free energies of adsorption by Dowex® Optipore L-493 were also estimated for each solute compound according to Equation 11, and the results are plotted in Figure 4 as a function of the alkyl chain length (see Table 2) for each prospective biofuel compound. As can be seen, for increasing carbon chain lengths the adsorption driving force is similarly increased. These data provide a straightforward means by which the recovery prospects of next generation biofuel compounds via solid-phase adsorption may be quantitatively compared. These predictions clearly illustrate that the prospective recovery of higher alcohols via solid-phase adsorption using

hydrophobic polymer resins is directly improved as the carbon chain length is increased, whereas alkyl chain branching renders a less significant effect.

With an understanding of the adsorption characteristics of each biofuel compound, the predicted uptake of those solutes can then be modeled under a variety of conditions to further explore the performance of polymeric resins in product recovery applications. For instance, in Figure 5 we compare the fraction of each compound that can be removed from aqueous solutions initially containing between 270 and 1350 mM (equivalent to between 20 and 100 g/L for n-butanol) of that solute by Dowex® Optipore L-493 as a function of the resin fraction. Again, it is observed that the recovery prospects are greatest as the alkyl chain length is increased and that among all prospective biofuels considered in this study, n-pentanol (the most hydrophobic compound) provides the greatest overall recovery potential. Conversely, the poor performance that is consistently exhibited with ethanol suggests that its adsorption using polymeric resins may not be a viable solution for its product recovery and purification.

Discussion

Although the application of solid-phase adsorbent materials for the recovery and purification of biological products from fermentation broths largely remains an emerging area of interest, there has been significant research into the use of this technology for the recovery of organic acid compounds, such as citrate (Jianlong et al., 2000), succinate (Davison et al., 2004), and ferulate (Ou et al., 2007), for example. The classic example, however, remains the recovery of lactate using ion-exchange resins (Cao et al., 2002; Dethe et al., 2006; Gonzalez et al., 2006; Rincon et al., 1997), and has been investigated

by utilizing a variety of different process configurations (Senthuran et al., 1997; Sun et al., 1999). In the case of organic acids, however, adsorption occurs via ionic interactions between the solute molecule and the ionic sites of weak base functionalized cation exchange resins. As previously discussed, the same mechanism is not valid for those molecules which remain non-ionizable at neutral conditions, including alcohols. In such cases, it is hydrophobic interactions between the solute molecule and the resin surface that instead drive the adsorption process. The strength of such interactions is governed by the relative hydrophobicity of both the solute and the resin matrix. It should be noted that hydrophobic interactions can alternatively be used to achieve separation of organic acids, however only at a pH that is well below the pKa of the solute of interest. For example, lactate (pKa 3.79) has been effectively recovered from aqueous broths via hydrophobic interactions with a neutral, poly(styrene-*co*-DVB) resin at pH 2 (Thang and Novalin, 2008). This requirement, of course, effectively limits the use of such approaches to only *ex situ* applications due to the incompatibility of such low pHs with most biocatalysts.

Overall, the best suited solutes for *in situ* product recovery using hydrophobic resins are those that themselves possess hydrophobic attributes. This result was consistent between both theoretical predictions and experimental measurements, and confirmed by both thermodynamic and equilibrium relationships. As was illustrated in Table 2, as the alkyl chain length of the alcohol solute is increased so too is its hydrophobic nature ($\log K_{O/W}$). Accordingly, among the biofuel compounds tested here, the greatest resin-aqueous equilibrium partitioning coefficients were achieved for the higher alcohols, such as 2-methyl-1-butanol, 3-methyl-1-butanol, and n-pentanol (Figure

2 and 3). This in turn provides the potential to recover a higher fraction of the total solute of these compounds from aqueous solutions, even for particularly concentrated solutions, by utilizing lower resin phase ratios (Figure 5). In fact, the resin fraction required to achieve a desired fractional uptake increases as the hydrophobic nature of the solute decreases. Of course, the recovery of less hydrophobic compounds, such as ethanol, from fermentation broths could still be achieved with the use of solid-phase adsorbent resins. However, as is illustrated in Figure 5, this could only be achieved through the use of considerably large resin fractions (and correspondingly high capital costs). Thus with increased carbon chain lengths, many second generation biofuels would make ideal targets for purification via adsorption using polymer resins, due to their increasingly hydrophobic nature. At the same time, resin phases comprised of non-polar monomeric units, such poly(styrene-*co*-DVB), have previously been demonstrated to exhibit the most hydrophobic characteristics (Nielsen and Prather, 2009). Furthermore, as can be seen when considering the available specific surface area data of Table 3, those resins with the highest surface area, such as Dowex® Optipore L-493 and SD-2, provided the greatest resin-aqueous equilibrium partitioning coefficients for n-butanol (Figure 1). It follows that as the specific surface area of the resin is increased so too is the total number of sites available for interaction with solute molecules.

Correlations between solute hydrophobicity and adsorption affinity on solid-phase materials have been well-documented in analytical chemistry research and serve as the basis for experimental estimation of $\log K_{OW}$ values via reverse phase high performance liquid chromatography (RP-HPLC) techniques, wherein hydrophobic resin materials typically constitute the stationary phase (Braumann, 1986; Dias et al., 2003). In short,

under identical separation conditions (i.e. isocratic mobile phase at a constant flow rate) the relative retention time between two analytes in RP-HPLC is found to be directly correlated with the relative $\log K_{O/W}$ values of those compounds (Griffin et al., 1999). Thus, just as we have used the relative hydrophobicity of two solutes to predict their respective adsorption equilibrium behavior on resin materials, the same ratio can be used to determine their respective retention times in RP-HPLC.

Suitable application of Langmuir isotherms would have implied the assumption that these branch and n-alcohols are adsorbed as monolayers at the resin surface, and that no interaction occurs between adsorbed molecules (Gokmen and Serpen, 2002). This further implies the existence of a homogeneously distributed adsorption surface. While it is expected that the chemical structure of each of the tested resin phases should be homogeneous, the same can not necessarily be said for the macrostructure of these porous materials. Although the Freundlich isotherm is largely an empirical relationship, this equation was found to most satisfactorily model the adsorption phenomena in the present study. Perhaps this is because the solutes do not strictly abide by the process of monolayer adsorption. Thus, although we are without adequate mechanistic evidence to fully characterize the surface phenomena, we can conclude that the adsorption of the selected branched and n-alcohols by the chosen resins behaved in a sufficiently non-ideal manner such that the Langmuir isotherms were found to be less suitable.

Negative values of the Gibb's free energy indicate that the adsorption of n-butanol (Figure 1), as well as other alcohol solutes examined (Figure 4), occurs via a spontaneous process. For solutes with unionized polar groups (such as alcohols at neutral pH, for example) it has been proposed that the Gibb's free energy of adsorption is dependent

upon contributions from the hydrophobic group and the nature of the hydrophilic group according to (Dynarowicz and Paluch, 1988):

$$\Delta G = \Delta G_p + \Delta G_h \quad (13)$$

where ΔG_p is the standard free energy of the polar group and ΔG_h is that of the hydrocarbon chain. Since ΔG_p corresponds to the hydroxyl group, its contribution should remain equivalent for each alcohol solute. Thus, as ΔG was observed to increase with increasing carbon chain length in Figure 4, we can assume that this increase was essentially due to contributions to ΔG_h alone. Accordingly, the observed linear trend suggests that ΔG_h was largely a direct function of carbon chain length for the series of both branched and n-alcohols considered here.

Whereas the focus of the present study has been on the characterization of resin materials for the *in situ* product recovery of both conventional and second generation biofuel compounds (all of which consisted of short-chain, saturated alcohols), we further predict that the same approach and proposed correlation would be equally well-suited for application with other hydrophobic fermentation products. Accordingly, we are interested in applying the present approach to further explore the prospects of integrated recovery of other biological products of interest, including natural flavor molecules such as vanillin (Hua et al., 2007) and benzaldehyde (Lomascolo et al., 2001; Lomascolo et al., 1999), as well as pharmaceutical building blocks (Straathof, 2003), in order to better assess the generic applicability of the present work.

Conclusions

The present study illustrates the utility of adsorbent polymer resin materials as effective separation devices for the *in situ* product recovery of emerging, second generation biofuel compounds. In fact, due to their elevated hydrophobicity (relative to n-butanol), 2-methyl-1-butanol, 3-methyl-1-butanol, and n-pentanol would each serve as better potential targets for recovery via adsorption using hydrophobic resins. Thus, recovery potential can accordingly be added to the list of plausible advantages motivating the further development of these compounds as alternative liquid biofuels. The proposed correlation which relates relative solute hydrophobicity to recovery potential provides a rapid and reliable means by which previously characterized resin materials may be screened for future applications for the *in situ* product recovery of second generation biofuels.

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Nomenclature

$b_{j,ri}$	Langmuir adsorption constant for solute j on resin r_i
$[A]_k$	concentration of solute A in phase k , mM
$[B]_k$	concentration of solute B in phase k , mM

367	$\Delta G_{j,ri}$	Gibb's free energy of adsorption of solute j on resin r_i , J mol ⁻¹
368	ΔG_h	contribution to the Gibb's free energy from the hydrocarbon group, J mol ⁻¹
369	ΔG_p	contribution to the Gibb's free energy from the polar group, J mol ⁻¹
370	$K_{F,j,ri}$	Freundlich isotherm constant of solute j on resin r_i , mmol kg ⁻¹ mM ⁻¹
371	$K_{O/W,j}$	octanol-water partitioning coefficient of solute j , mM mM ⁻¹
372	$K_{R/W,j,ri}$	resin-water equilibrium partitioning coefficient of solute j for resin r_i ,
373		mmol kg ⁻¹ mM ⁻¹
374	$K_{R/W,j,ri,max}$	maximum resin-water equilibrium partitioning coefficient of solute j for
375		resin r_i , mmol kg ⁻¹ mM ⁻¹
376	$L_{j,ri}$	specific loading of solute j on resin r_i , mmol kg ⁻¹
377	$L_{j,ri,max}$	maximum specific loading of solute j on resin r_i for Langmuir isotherm,
378		mmol kg ⁻¹
379	m_{ri}	mass of the resin phase r_i , kg
380	$n_{j,ri}$	Freundlich exponent of solute j on resin r_i
381	R	ideal gas constant, 8.314 J mol ⁻¹ K ⁻¹
382	T	temperature, K
383	t_0	time at initial condition, h
384	t_{eq}	time at equilibrium, h
385	V_{aq}	volume of the aqueous phase, L
386	X_{ri}	fraction of resin r_i , kg L ⁻¹

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388 **References**

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Figure Captions

Figure 1. Experimental and best-fit Freundlich adsorption isotherms of n-butanol with Dowex Optipore L-493 (solid triangles), Dowex Optipore SD-2 (open squares), Diaion HP-20 (solid circles), Diaion HP-2MG (open triangles), Dowex M43 (solid squares), and Hytrel 8206 (open circles). Best-fit parameter estimates and predicted Gibb's free energies of adsorption for each resin are listed in the inset table.

Figure 2. A comparison of experimental resin-aqueous equilibrium partitioning coefficients with those values predicted by the proposed model for various resins and a series of second generation biofuel compounds, including: ethanol (open diamond), n-propanol (filled square), iso-propanol (open inverted triangle), iso-butanol (filled diamond), 2-methyl-1-butanol (open upright triangle), 3-methyl-1-butanol ('X'), and n-pentanol (star). Dashed lines indicate $y = x$.

Figure 3. Experimental and best-fit Freundlich adsorption isotherms of ethanol (open triangles), iso-propanol (open diamonds), n-propanol (solid circles), iso-butanol (open squares), 2-methyl-1-butanol (solid diamonds), 3-methyl-1-butanol (open circles), and n-pentanol (solid squares) using Dowex® Optipore L-493. Best-fit parameter estimates for each compound are listed in the inset table.

Figure 4. Predicted Gibb's free energies of adsorption for each of the investigated biofuels by Dowex® Optipore L-493 as a function of their carbon number. Solid shapes represent *n*- alcohols whereas open shapes are branched alcohols.

Figure 5. Predicted fractional adsorption as a function of the resin fraction for Dowex® Optipore L-493 with initial solute concentrations of 270, 675, or 1350 mM for ethanol (solid circles), iso-propanol (dashed line), n-propanol (open circles), iso-butanol (dotted line), n-butanol (open squares), 2-methyl-1-butanol and 3-methyl-1-butanol (solid line), and n-pentanol (open triangles).