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Improved Hydrodynamic Model for Wetting Efficiency, Pressure Drop, and Liquid Holdup in Trickle-Bed Reactors

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An improved hydrodynamic model is developed for estimating wetting efficiency, pressure drop, and liquid holdup in trickle-bed reactors. The model is based on the hydrodynamic model presented in Alopaeus et al. [Alopaeus, V.; Hynynen, K.; Aittamaa, J.; Manninen, M. Modeling of Gas−Liquid Packed-Bed Reactor with Momentum Equations and Local Interactions Closures. *Ind. Eng. Chem. Res.* **2006**, *45*, 8189.], which is extended to take into account partial wetting of the packing. In addition, the applicability of the 1D model for three-dimensional situations is considered in the process of model development. The wetting efficiency model is formulated on the basis of dimensional analysis and carrying out systematic tests with varying combinations of dimensionless groups. In addition, the wetting efficiency model is not evaluated solely on the wetting efficiency data, but also it is tested systematically with the hydrodynamic model. Furthermore the consistency of the model characteristics to common experimental observations is discussed. Finally, the model's ability to predict wetting efficiency, dimensionless pressure drop, and liquid saturation was compared to other existing models and improvements were found in all areas. The resulting hydrodynamic model can be used equally as a tool for design and modeling of large scale industrial reactors as well as a tool for complicated three-dimensional simulations.

1. Introduction

Trickle-bed reactors are widely used three-phase reactors. Important applications can be found in petroleum, petrochemical, and chemical industries, in waste treatment, and in biochemical and electrochemical processing.[2] The economical aspects and constantly tightening environmental regulations are the driving forces behind the continuous research aiming to improve trickle-bed reactor performance.

On the hydrodynamic level, the performance of a trickle-bed reactor is generally thought to be influenced mainly by the following three parameters: pressure drop, liquid holdup, and wetting efficiency. Consequently, reliable models of these parameters are required for trickle-bed reactor design and scale-up. The first two have been subjects of research for decades, but the importance of the wetting efficiency was only thoroughly acknowledged in the last half of the 1970s.[3] After that, research on wetting efficiency has been extensive.[3−25] The main concern has, however, been on wetting efficiency correlations or on the effect of wetting efficiency on reactor performance, and not on how to relate wetting efficiency to the modeling of packed-bed hydrodynamics. On some occasions the wetting efficiency has been used to emphasize the effect of the capillary force on liquid distribution,[26,27] but the "double-slit"[28,29] and the "four-slit"[30] models are so far the only hydrodynamic models having wetting efficiency incorporated within them.

It has been generally thought that in commercial reactors, the catalyst particles are completely wetted, that is, the wetting efficiency is close to one.[31] However, the hydrodynamic models, as well as reactor scale-up, are generally based on laboratory scale reactors, where the actual velocities are usually substantially lower than in industrial reactors, which implies lower wetting efficiency. This problem originates from the need for the laboratory scale reactors to match the liquid hourly space velocity (LHSV = volumetric feed/catalyst volume) of the commercial units.[25,32] It is clear that difference in catalyst wetting in different scales is a potential source for reactor performance misprediction during scale-up. Sufficient wetting efficiency in industrial scale reactors is, however, another factor, which may present problems in the future. As an important example, the tightened regulations concerning the allowable sulfur content in refinery products and the degree of hydrotreating of heavy oils requires industrial reactors to operate with higher conversions. One way of meeting this goal is to use longer residence times, which in turn means lower liquid flow rates and, consequently, deteriorated wetting efficiencies.[25] In case of exothermic reactions, such as various hydrotreatment operations encountered in the petroleum industry, wetting efficiency plays also a significant role in reactor safety—incomplete wetting of the catalyst can increase the reaction rate of a gas limited reaction,[33−35] which results in excess heat generation with no liquid phase to recover it and potential reaction run-away within the bed.

2. Wetting Efficiency

The external wetting efficiency of the catalyst, f_e, hereafter referred simply as the wetting efficiency, is generally defined as the fraction of catalyst surface covered with flowing liquid.[4,6,7,9,15,16,18,22,36] The remaining fraction of the catalyst $(1 - f_e)$ is either covered with a stagnant liquid film or it is dry. Some authors separate between the fractions of stagnant liquid and dry zones,[17] but we consider here only the separation between the flowing liquid zone and the stagnant liquid/dry zone, which is sufficient for the modeling purposes. Measurement

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Table 1. Literature Correlations for the Wetting Efficiency, f_e

source	correlation	additional information
3	$f_e = \sqrt{D_{TP}/D_{LF}} = 1.0 - \exp\left[- 1.35 Re_L^{0.333} Fr'^{0.235}_L We'^{-0.170}_L \left((a_t d_p^2)/cm/\varepsilon^2\right)^{-0.0425}\right]$ $f_e = \sqrt{D_{TP}/D_{LF}} = 1.0 - \tanh\left[0.664 Re_L^{0.333} Fr'^{0.195}_L We'^{-0.171}_L \left((a_t d_p^2)/cm/\varepsilon^2\right)^{-0.0615}\right]$	tracer method; only 26 data points were used to fit 5 parameters
6	$f_e = 1.617 Re_L^{0.146} Ga_L^{-0.071}$ $f_e = 1.02 S_{L,dyn}^{0.244}$	tracer method
7	$f_e = 0.77\left(L_m/kg/ms^2\right)^{0.1}$	the background of the correlation was not reported
13	$f_e = \sqrt{D_{TP}/D_{LF}} = 1 - \exp\left(- 118 (U_L/m/s)^{0.635}\right)$	tracer method
1	$f_e = 1 - 25.353 / \quad e_L^{0.96}$ 180>Re_L>35	tracer method
15	$f_e = 1.104 (Re_L^*)^{1/3}\left[1 + [(\Delta P/\Delta L)/(\rho_L g)] / Ga_L^*\right]^{1/9}$	tracer method; high pressure
16	$f_e = 3.38 Re_L^{0.222} Re_G^{-0.083} (Ga'_L)^{-0.512}$	tracer method; one gas−liquid system generalization based on analogy with typical wetting efficiency correlations
38	$f_e = 1.301 + 0.0739 \ln(U_L/(m/s))$ $0.0002 < U_L < 0.01 m/s$	reaction rate method; measurements in Herskowitz[36]
39	$f_e = 1 - \exp[-4.265 \times 10^{-2} (Re_L^*)^{0.745} (Re_G^*)^{0.079}]$ $6.71 < Re_L^* < 117.90$ $32.00 < Re_G^* < 204.19$	reaction rate method
40	$f_e = 0.83S + 0.17$ $1/S = 1 + \exp[-\sum_{j=1}^{8} \omega_j H_j]$ $1/H_j = 1 + \exp[-\sum_{i=1}^{6} \omega_{ij} U_i]$ the normalized input groups (U_i) and connectivity weights (ω) are presented in Table 3 of the corresponding reference	neural network correlation

techniques for wetting efficiencies are presented for example in ref 23 and ref 25.

The earlier wetting efficiency measurements suffer from neglecting the effect of prewetting procedure on the flow structure. Kan and Greenfield[37] demonstrated that, depending on the flow history, there is a possibility of multiple hydrodynamic states, which probably explains part of the variation in the results. Another problem is that before Ring and Missen[13] all models were based solely on measurements at atmospheric pressure. Table 1 presents literature correlations for wetting efficiency.

Wetting efficiency is affected by several operation parameters. Some of these have a clear effect on the wetting efficiency whereas for others the effect is less evident. A general outline of the effect of some of the main operation parameters is given below based on the current knowledge.

Liquid Flow Rate. According to number of studies, increase in liquid flow rate has a positive effect on wetting efficiency.[3−7,12,13,15,18,21,22,36,39]

Gas Flow Rate and Density. The effect of gas flow rate to wetting has been found to be improving,[5,15,18,22] decreasing,[9] or unclassifiable.[12,14,17] The divergence in the results derives from the complicated effect of gas flow rate on the trickle-bed hydrodynamics: increase in gas flow rate decreases liquid holdup,[12,16,18] but at the same time it also decreases channeling and improves the liquid spreading over the catalyst particles.[21]

Size and Shape of Particles. In general decreasing particle size has been found to improve wetting,[4,16,21,25] although contradictory[5,14] or even unclassifiable[22] results can also be found. From the theoretical point of view, the capillary pressure forces, which are driving forces for liquid spreading, increase with decreasing particles as well as with decreasing porosity.[41,42] Particle shape has not been found to influence wetting.[15,25]

Solid−Liquid Affinity. Baussaron et al.[25] found that with liquid superficial velocities lower than 0.002 m/s solid−liquid affinity controls wetting, but at higher flow rates wetting is controlled by hydrodynamics. El-Hisnawi et al.[6] found that surface tension is insignificant in the low interaction (trickling) flow regime, but became important in the high interaction (pulsing) regime.

3. An Algebraic Model for Trickle-Bed Reactors

In our earlier work[1] we presented a one-dimensional algebraic model for trickle-bed hydrodynamics. Existing interaction models were analyzed and improved models, based on analysis of particle scale geometry, were presented. A detailed description of the one-dimensional solution procedure is presented in Alopaeus et al.[1] and thus only the essential features of the model are presented here.

For a two-phase flow through a packed-bed with uniform liquid feed, the following, algebraic system of equations can be written:

$$\frac{\Delta P}{\Delta L} = \rho_L g + \frac{F_{int,L}}{\theta_L} \tag{1}$$

$$\frac{\Delta P}{\Delta L} = \rho_G g + \frac{F_{int,G}}{\theta_G} \tag{2}$$

where $F_{int,L}$ and $F_{int,G}$ represent the total force exerted on the liquid and the gas phase, respectively, due to the interaction forces between the three phases present in the medium.

3.1. Interaction Forces. When wetting is included, the total interaction forces exerted on gas and liquid phases can be written as follows:

$$F_{int,G} = -f_e F_{GL} - (1 - f_e) F_{GS} \tag{3}$$

$$F_{int,L} = f_e (F_{GL} - F_{LS}) \tag{4}$$

where the magnitude of the phase interaction forces is related to wetting efficiency, f_e. Similar approach has also been suggested by Iliuta and Larachi.[43] It is assumed here that the stagnant liquid is held in place by forces other than the phase interaction forces, for example, capillary forces. Because this liquid film remains stagnant, modeling of these additional forces can be avoided by assuming that gas interacts directly with solid, and liquid phase experiences no interactions whatsoever at stagnant regions. If perfect wetting is assumed, eqs 3 and 4 reduce to the form used in Alopeus et al.[1] In that work the following equations for gas−liquid and liquid−solid interaction forces were presented:

$$F_{GL} = \theta_G \left\{ \frac{E_{\mu,G}(1-\theta_G)^2 \mu_G}{\theta_G^2 d_p^2} + \frac{E_{\rho,G}(1-\theta_G)\rho_G |\bar{u}'_G - \bar{u}_L|}{\theta_G d_p} \right\} \times (\bar{u}'_G - \bar{u}_L) \quad (5)$$

$$F_{LS} = \theta_L \left\{ \frac{E_{\mu,L}(1-\varepsilon)^2 \mu_L}{\theta_L^2 d_p^2} + \frac{E_{\rho,L}(1-\varepsilon)\rho_L |\bar{u}_L|}{\theta_L d_p} \right\} \bar{u}_L \quad (6)$$

where $E_{\mu,i}$ and $E_{\rho,i}$ are the phase specific Ergun constants and $\bar{u}'_G - \bar{u}_L$ is the gas−liquid slip velocity, where the modified gas velocity is

$$\bar{u}'_G = \frac{\bar{u}_G}{\alpha} \quad (7)$$

In analogy with the gas−liquid interaction, we use the following equation for the gas−solid interaction force:

$$F_{GS} = \theta_G \left\{ \frac{E_{\mu,G}(1-\theta_G)^2 \mu_G}{\theta_G^2 d_p^2} + \frac{E_{\rho,G}(1-\theta_G)\rho_G |\bar{u}'_G|}{\theta_G d_p} \right\} \bar{u}'_G \quad (8)$$

In totally dry bed eq 8 simplifies to the original one-phase Ergun equation.

3.2. Phase Tortuosity. The Ergun parameters are assumed to be related to tortuosities, in the spirit of the slit model.[28,29,44]

$$E_{\mu,i} = 72 T_i^2 \quad (9)$$

$$E_{\rho,i} = 6 f_\tau T_i^3 \quad (10)$$

Tortuosities are phase specific and depend on the gas saturation:

$$T_G = \frac{T_0 + 1}{2} + \alpha \left(\frac{T_0 + 1}{2} - 1 \right) \quad (11)$$

$$T_L = T_0 A^{(\alpha^B)} \quad (12)$$

where A and B are optimized parameters and T_0 can be obtained from one-phase Ergun parameters.[44] Here we have used the values of 180 and 1.8 for empty-bed Ergun constants E_μ and E_ρ, respectively, in which case a value of 1.58 is obtained for T_0. The gas-phase tortuosity model is the same as in Alopaeus et al.,[1] but the liquid-phase tortuosity has been modified. The previously presented liquid tortuosity model was found to perform well if the bed was assumed completely wetted, which was the basic assumption in our previous work.[1] In 3D CFD studies it was found, however, that the liquid tortuosity model overpredicts F_{LS} in cases where the liquid front penetrates into parts of the bed with low liquid saturation. At higher liquid saturations the new liquid-phase tortuosity model gives similar predictions as the previous model. The new formulation is, however, improved so that the liquid-phase tortuosity does not approach infinity as liquid saturation approaches zero, which is not physical and would cause problems in more complicated CFD simulations.

3.3. Wetting Efficiency. The wetting efficiency is a too complex phenomenon to be modeled solely on phenomenological reasoning. Instead, we will use a mechanistic model, with relatively few adjustable parameters. We feel that in the case of models with a high number of adjustable parameters (e.g., the neural network models) the comparison between the characteristics of the phenomenon and the behavior of the model becomes more unclear. In the case of a relatively simple model this type of examination can be performed with ease as will be shown later.

For the model to have accurate predictive capabilities (for example when the model is used outside the realm of the experimental area used for fitting) the variables that are used in the model should have a clear physical meaning or they should be based on dimensional similitude. The latter approach is used here. The dimensionless groups included into the analysis are chosen so that they are physically relevant in two-phase flow through a packed-bed. The following dimensionless groups, N_i, are tested during the optimization process:

- Packed bed capillary number: $\mathrm{Ca}^* = U_L \mu_L / \varepsilon\sigma$
- Modified Eötvös number: $\mathrm{Eö}^* = \rho_L g d_p^2 \varepsilon^2 / [\sigma(1-\varepsilon)^2]$
- Gas and liquid Froude numbers: $\mathrm{Fr}_i = U_i / \sqrt{g d_p}$
- Packed bed gas and liquid Galileo numbers: $\mathrm{Ga}_i^* = \rho_i^2 g d_p^3 \varepsilon^3 / [\mu_i^2 (1-\varepsilon)^3]$
- Liquid Ohnesorge number: $\mathrm{Oh}_L = \mu_L^2 / \sqrt{\sigma d_p \rho_L} = \sqrt{\mathrm{Ca}/\mathrm{Re}_L}$
- Packed bed gas and liquid Reynolds numbers: $\mathrm{Re}_i^* = \rho_i d_p U_i / (\mu_i (1-\varepsilon))$
- Gas and liquid Stokes numbers: $\mathrm{St}_i = \mu_i U_i / (\varepsilon \rho_i g d_p^2)$
- Liquid Weber number: $\mathrm{We}_L = U_L^2 d_p \rho_L / (\varepsilon^2 \sigma) = \mathrm{Ca} \cdot \mathrm{Re}_L$
- Lockhart−Martinielli parameter: $\chi = \sqrt{(\Delta P/\Delta L)_G / (\Delta P/\Delta L)_L}$ We are seeking for an optimal combination of dimensionless numbers determining the wetting efficiency in the following form:

$$f_e = C_0 \prod_{i=1}^{n} N_i^{C_i} \quad (13)$$

where C_i ($i \in [0,n]$) are the parameters to be optimized, N_i refers to a dimensionless group, and n is the total number of dimensionless groups included in the model. From the above dimensionless groups only the groups including either gas or liquid flow rate have the potential to go to zero in trickle-bed operation conditions. In either case $N_i^{C_i}$ would go either to zero ($C_i > 0$) or to infinity ($C_i < 0$), of which the latter case corresponds to perfect wetting ($f_{e,max} = 1$ and thus if $f_e > 1$ then $f_e = 1$). The assumption that the wetting efficiency is either 1 or 0 in the case of no gas flow is not physical. Thus if N_i includes the gas velocity, the form $(1 + N_i)^{C_i}$ is used instead of $N_i^{C_i}$ in eq 13. The modified form is physically sound: the effect of gas flow simply vanishes in the case of no gas flow. For the liquid flow rate it is likely that C_i will be positive[3−7,12,13,15,18,21,22,36,39] and thus the wetting efficiency goes to zero along with the liquid flow rate. This is in accordance with the determination of the wetting efficiency: the fraction of catalyst surface covered with flowing liquid.

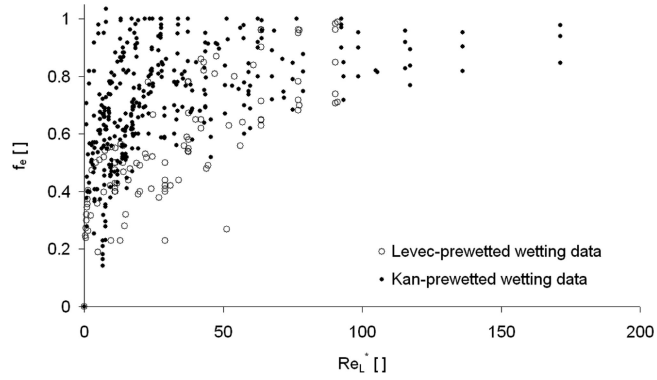

Figure 1. Comparison between (●) the Kan- and (○) the Levec-prewetted data as function of packed-bed liquid Reynolds number.

4. Experimental Databases

4.1. Optimization Database. The optimized model parameters are A and B in the liquid phase tortuosity model, eq 12, and C_i in the wetting efficiency model, eq 13. The database used in the optimization included altogether 252 experimental

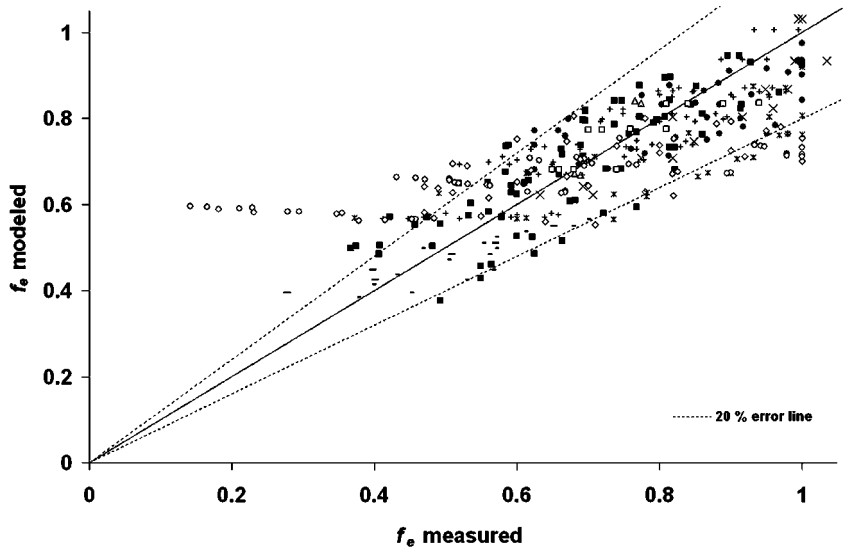

Figure 2. Parity plot between the modeled wetting efficiencies and literature data. Data used in optimization: (●) Ald-Dahhan and Duduković,[15] (■) Baussaron et al.,[25] (×) Colombo et al.,[4] (+) Kundu et al.,[22] (∗) Lakota and Levec,[12] (-) Ring and Missen,[10] and (—) Ring and Missen.[13] Data not included to the optimization: (○) Alicilar et al.,[14] (△) van Houwelingen et al.,[24] (□) Lazzaroni et al.,[9] and (◇) Specchia et al.[5]

Table 2. Parameters for the Final Hydrodynamic Model with Group 1 to 4 Wetting Efficiency Models

		number of dimensionless groups in the wetting efficiency model			
		$n = 1$	$n = 2$	$n = 3$	$n = 4$
dimensionless groups	N_1	Fr_L	$Re_L{}^*$	$Re_L{}^*$	$Re_L{}^*$
	N_2		Eö*	Eö*	Eö*
	N_3			$Ga_G{}^*$	$Ga_G{}^*$
	N_4				$(1 + Fr_G)$
fitted parameters	A	9.908	3.719	3.565	3.592
	B	2.515	1.182	1.134	1.140
	C_0	1.507	0.419	0.335	0.335
	C_1	0.090	1.229	0.185	0.185
	C_2		1.343	−0.187	−0.188
	C_3			0.027	0.027
	C_4				−0.014
wetting efficiency	$\langle e_{f_e} \rangle$	5.25	4.69	4.45	4.44
	STD_{e,f_e}	3.95	3.22	2.98	2.97
	$B(X)_{f_e}$	−0.014	0.003	−0.001	−0.002
dimensionless pressure drop	$\langle e_{\Delta P/Z} \rangle$	19.07	18.61	18.74	18.73
	$STD_{e,\Delta P/Z}$	14.50	14.99	15.69	15.65
	$B(X)_{\Delta P/Z}$	0.007	0.078	0.026	0.0294
liquid saturation	$\langle e_{S_L} \rangle$	5.56	5.44	5.43	5.43
	STD_{e,S_L}	6.17	6.12	6.16	6.15
	$B(X)_{S_L}$	0.020	0.017	0.017	0.017

points for pressure drop,[45−51] 405 points for liquid holdup,[4,12,13,16,18,21,45−49,51−53] and 353 points for wetting efficiency.[4,10,12,13,15,22,25] From the 353 wetting efficiency experimental points only 248 were used in the wetting model parameter optimization, which included the works of Al-Dahhan and Duduković,[15] Baussaron et al.,[25] Colombo et al.,[4] Kundu et al.,[22] Lakota and Levec,[12] and Ring and Missen.[10,13] The remaining 105 experimental points were not used in the optimization due to uncertainties in the experimental conditions. These points include the data of Alicilar et al.,[14] van Houwelingen et al.,[24] Lazzaroni et al.,[8] and Specchia et al.,[5] which were all excluded due to unknown porosity of the bed. In the comparison to model predictions (Table 6 and Figure 2), estimated bed porosities were used. For the sake of consistency all wetting efficiency data points that were obtained from tracer method using diffusivity ratio were transformed to the form

$$f_e = \sqrt{\frac{D_{TP}}{D_{LF}}}$$

4.2. Levec-Prewetted Wetting Efficiency Database. In addition to the wetting efficiency data presented above, measurements with the Levec-prewetting method have been reported in the literature.[18−21,24] From Luciani et al.[20] the wetting efficiencies measured with CMC-solutions are excluded, since Baussaron et al.[25] have shown that with fluids other than air and water, the method severely overpredicts the wetting efficiency. In González-Mendizabal et al.[39] the prewetting method is not reported, but in light of their later work[18,20] it is likely that the Levec-prewetting method has been used and thus the parts of their data we could obtain is included in the Levec-prewetted database. Wetting efficiencies from the Levec-prewetted experiments were not included in the model optimization or into the model performance analysis, since in a Levec-prewetted bed flow structure is more dependent on flow history, whereas the Kan-prewetting method results in more repeatable flow behavior. The difference is larger with low liquid velocities and the wetting efficiencies come closer together as liquid flow rate increases.[23,24] The matter is demonstrated in Figure 1, where the Kan- and Levec-prewetted data are plotted as a function of the packed-bed liquid Reynolds number. Since the liquid flow structure with Kan- and Levec-prewetting methods vary, the resulting wetting efficiencies cannot be modeled with a single model.

5. Development of the Wetting Efficiency Model

The influence of the number of dimensional groups included into the wetting efficiency model is evaluated on the basis of how well the resulting hydrodynamic model predicts the experimental results of the database. First the parameters for the wetting efficiency model are optimized on the basis of the 248 experimental points. Then the corresponding tortuosity model parameters are optimized using the 252 pressure drop and 405 liquid holdup experimental points. The goodness of fit is evaluated by calculating the sum of the mean relative errors, $\langle e_X \rangle$, for the wetting efficiency (f_e), dimensionless pressure drop ($\psi_{\Delta p}$), and liquid saturation (S_L). The following expression for $\langle e_X \rangle$ was used:

$$\langle e_X \rangle = \frac{100\%}{N} \sum_1^N \left| \frac{X_{expt,i} - X_{calcd,i}}{1 + X_{expt,i}} \right| \qquad (14)$$

where $1 + X_{expt,i}$ is used as a denominator to prevent overemphasizing the smallest measured values. In addition to

Table 3. Characteristics of the Wetting Efficiency Models When Different Number of Dimensionless Groups (N) Are Included in the Model

		resulting exponent of the variable in the wetting model				effect as the value of the variable increases
		$n = 1$	$n = 2$	$n = 3$	$n = 4$	
liquid-phase properties	U_L	0.258	0.179	0.185	0.185	increasing
	ρ_L	0	0.031	−0.002	−0.003	insignificant
	μ_L	0	−0.179	−0.185	−0.185	decreasing
gas-phase properties	$1 + U_G$	0	0	0	−0.028	decreasing
	ρ_G	0	0	0.054	0.054	increasing
	μ_G	0	0	−0.054	−0.054	decreasing
phase interaction	σ	0	0.148	0.187	0.188	improving
packing properties	ε^a	0.000	−0.296	−0.293	−0.295	increasing
	$(1 - \varepsilon)$*	0	0.117	0.108	0.110	
	d_p	−0.129	−0.117	−0.108	−0.096	decreasing

[a] Term including ε and $1 - \varepsilon$ were not expanded, but treated separately.

Table 4. Effect of the Change in the Operation Parameters to the Value of the Wetting Efficiency

			$\Delta f_e/f_{e,median}100\%$	
operation parameter	X_{median}	$\Delta X = (X_{max} - X_{min})/10$	$X = X_{median} - \Delta X$	$X = X_{median} + \Delta X$
U_L [mm/s]	3.65	9.1	−78.04	26.00
ρ_L [kg/m^3]	998	55.3	0.02	−0.01
η_L [mPas]	1.00	3.5	33.09	−24.25
U_G [cm/s]	8.0	15.6	0.28	−1.21
ρ_G [kg/m^3]	1.19	0.61	−3.78	2.24
η_G [μPas]	18.2	0.55	0.17	−0.16
σ [mN/m]	72.0	0.66	−1.79	1.66
ε [ ]	0.400	0.023	2.19	19.53
d_p [mm]	3.00	0.63	2.62	−2.07

Table 5. Comparison of the Performance of the New Hydrodynamic Model to the Models of Attou et al.,[54] Tung and Dhir,[55] and Sáez and Carbonell[56] Based on Predicted Pressure Drop, $\Delta p/Z$, and Liquid Saturation, S_L

	new model	Attou et al.[54]	Tung and Dhir[55]	Sáez and Carbonell[56]
$\langle e_{\Delta P/Z} \rangle$	18.73	26.82	27.86	21.76
$STD_{e,\Delta P/Z}$	15.65	14.26	15.07	12.72
$B(X)_{\Delta P/Z}$	0.029	1.023	1.069	0.336
$\langle eS_L \rangle$	5.43	8.62	7.92	7.07
STDe,S_L	6.15	6.84	7.19	6.91
$B(X)S_L$	0.017	0.094	0.083	0.079

Table 6. Comparison of the Available Wetting Efficiency Correlations to the New Model (Group 4 Wetting Efficiency)

	$\langle e_{f_e} \rangle$	$STD_{e,fe}$	$B(X)_{f_e}$	applicability to the data [%]
new model	5.65	5.35	0.00	100.00
Alicilar et al.[14]	26.14	8.20	0.56	13.88
Burghardt et al.[16]	13.43	8.17	0.27	81.59
El-Hisnawi et al.[6]	6.50	6.16	−0.10	100.00
González-Mendizibal et al.[39]	17.32	7.28	0.41	25.50
Herskowitz[36]	10.68	9.22	−0.30	100.00
Herskowitz and Smith[7]	11.33	9.51	−0.33	100.00
Larachi et al.[40]	8.56	7.94	−0.10	100.00
Mills and Duduković[3]	10.78	9.21	−0.32	100.00
Ring and Missen[13]	10.97	7.28	0.21	58.07

liquid saturation and wetting efficiency, also 20% of the measured dimensionless pressure drops within the optimization database are less than one.

Besides the mean relative error, also other measures are illustrative when the model performance is evaluated. The sum of all errors is used to examine if the model is biased:

$$B(X) = \frac{1}{N}\sum_{1}^{N}(X_{expt,i} - X_{calcd,i}) \tag{15}$$

For an unbiased model, $B(X)$ should be close to zero.

The standard deviation of the relative error around the mean relative error, STD_e, can be used to compare the ability of the models to describe correctly the trend of the modeled property.

$$STD_e = 100\sqrt{\frac{1}{N-1}\sum_{1}^{N}\left(\left|\frac{X_{expt,i} - X_{calcd,i}}{1 + X_{expt,i}}\right| - \langle e_X \rangle\right)^2} \tag{16}$$

The above statistical numbers are used to evaluate the goodness of the hydrodynamic models. The same measures are also used for literature model evaluation.

The search for the optimum wetting model was started by testing wetting efficiency models involving only a one-dimensional group in eq 13. The four models that produced the best fit against the experiments were then selected for improvement by adding a second dimensionless group to the model. The same procedure was then repeated in the attempt to improve the four best wetting efficiency models having two dimensionless groups and so on. In principle, this analysis could be carried out also in the opposite way: First include all the dimensionless groups into the model and simultaneously fit all the parameters. Then by looking at the confidence intervals and cross-correlations between the parameters, remaining dimensionless groups could be discarded from the model one by one. However, optimizing a large set of parameters to scattered data is extremely difficult, and it is almost inevitable that the optimization algorithm would end up in a local minimum. Starting with a small number of parameters and testing all viable combinations is a more robust method.

6. Results and Discussions

Table 2 presents the results for the best hydrodynamic models, with one to four dimensionless groups included into the wetting efficiency model. The most significant improvement can be seen between wetting efficiency models with one and two dimensionless groups, after which the improvement is less notable. The qualitative behavior of the model and its extrapolative properties outside the majority of the experimental points are, however, influenced by the augmentation of dimensionless groups to the wetting efficiency model. This will be considered in more detail in the following section.

6.1. Characteristics of the Wetting Efficiency Model. The tested wetting efficiency models are rated, besides looking at the prediction accuracy at the data points, according to their capability to reproduce the known trends in a sensitivity analysis. This is of utmost importance since most data points in practically all chemical engineering systems are obtained in moderate temperatures and pressures using small-scale laboratory equipment, whereas these models should be extendable to large-scale, high-pressure, and high-temperature applications.

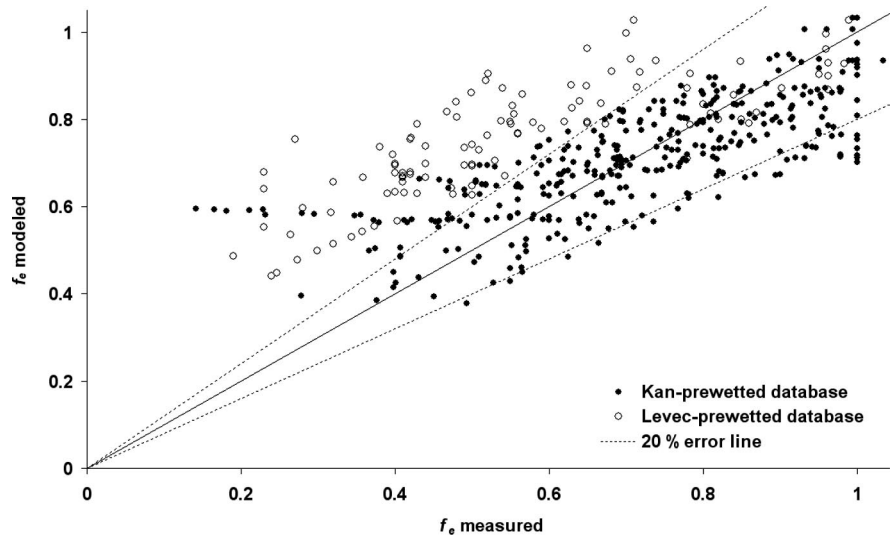

Figure 3. Parity plot between the model predictions and the experimental points obtained in a (○) Levec-prewetted bed and the experimental points obtained in a (●) Kan-prewetted (or equivalent) bed.

The effect of various operation parameters on wetting can be evaluated by expanding the dimensionless groups and collecting the exponents for each physical variable separately. This has been done in Table 3. In addition, the sensitivity of the predicted wetting efficiency to the operation parameters is presented in Table 4. The optimization database includes experimental points for the pressure drop, liquid holdup, and wetting efficiency. The wetting efficiency model with four dimensionless groups has been used to estimate the wetting efficiency. The sensitivity is estimated as a percentage change in the wetting efficiency as the value of a parameter is changed by a value that is equal to one tenth of the total range of that parameter in the optimization database. The reference value, $f_e = 0.75$, is calculated from the median values of the operation parameters, which are presented in Table 4. The temperature and pressure are not directly included into the wetting efficiency model, but they have an effect through changes in the phase physical properties and also through vapor−liquid equilibrium.

Although based on the results presented in Table 2, the inclusion of more than two-dimensional groups does not seem to improve the model, examination of Table 3 suggests otherwise. The wetting efficiency model does not describe all the known trends of wetting efficiency properly, until the inclusion of the fourth dimensionless group. This may prove significant once the model is used out of the operation range used in the model development.

By considering the characteristics of the model its consistency with the experiments can be compared:

Liquid Phase Properties. Among the liquid phase properties only velocity has been studied. The model is consistent with majority of the available research, predicting a strong positive influence of liquid velocity on wetting efficiency. The model also predicts a significant decreasing influence of increasing liquid viscosity on wetting efficiency.

Gas Phase Properties. It is interesting to notice that only models with three or more dimensional groups include the effect of gas phase properties. Only the model with four dimensionless groups show the contradictory effect of the gas velocity: increase in gas velocity decreases wetting efficiency, but at the same time pressure drop increases, which in turn has a positive effect on wetting efficiency through increased gas density. This observation could explain the inconsistent conclusion made from the experimental results. The effect of gas velocity is small. Gas density has a stronger effect, especially at low densities.

Gas−liquid Surface Tension. Only El-Hisnawi et al.[6] have reported any conclusions concerning the effect of gas−liquid surface tension to the wetting efficiency. They found surface tension to have a positive effect on wetting efficiency, which is consistent with the predictions of the present model.

Bed Properties. The model predicts an increase in wetting efficiency with decreasing particle size or bed porosity. Both are consistent with the experiments and also with theoretical considerations.

6.2. Performance of the Final Two-Phase Interaction Model. In this section the ability of the model to predict pressure drop, liquid holdup, and wetting efficiency is compared to the other existing models. The hydrodynamic model having four dimensionless parameters included into the wetting efficiency model is used in all comparisons.

In Table 5 the model performance is compared to the two-phase interaction models of Attou et al.[54] and Tung and Dhir[55] and to the permeability model of Saéz and Carbonell.[56] The permeability model has been found to perform well in pressure drop and liquid saturation predictions,[57,58] which is confirmed here. The robustness of the permeability model, however, is slightly worse than the robustness of the other models, including the new model. Using *fsolve* algorithm provided by Matlab,[59] with the same starting value of $\alpha = 0.5$ for all the experimental points, the permeability model did not converge for all the experimental points, whereas the other tested models did. From Table 5 we can see that the new model further improves the dimensionless pressure drop and liquid saturation predictions.

In Table 6 the results of the new wetting efficiency model is compared to the available literature wetting efficiency correlations. The statistical numbers are calculated on the basis of all experimental points, including those that were excluded from the wetting efficiency model parameter optimization due to unknown porosities. The correlation of Al-Dahhan and Dudukovi\'c[15] is not included to the comparison, since only 41 wetting efficiency data points (about 11% of all data) included information about pressure drop, which was required in their model. Of these 41 data points, 37 were their own data which was also used to fit the parameters of their model. The rightmost column shows the percentage of the data that falls into the limiting

operation parameters of the model. The correlations of Alicilar et al.,[14] Burghardt et al.,[16] and González-Mandizabal et al.[39] can be used only for the limited number of experimental points. Therefore, the values for STD_e and $B(X)$ are not as reliable for these cases. Table 6 shows that the new model improves the wetting efficiency prediction significantly when compared to the other tested models.

Figure 2 presents the parity plot between the experiments and the modeled wetting efficiencies. The black marks are the experimental points that have been used in the model optimization. The filled gray marks represent the experiments that were excluded from the optimization, due to unknown porosity. The model predicts the trend of the data well for most of the data points. The experimental points of Alicilar et al.[14] make an exception. They obtained the wetting efficiency values from tracer data, but they used the less used theory of Schwartz et al.,[60] instead of the diffusivity ratios, which might explain the distinctly different trend in comparison to the rest of the data.

In Figure 3 the parity between the model and the Levec-prewetted bed database, as well, the parity between the model and the wetting efficiency database are shown together. The differences between the two prewetting methods are consistent with the observations of van Houwelingen.[23] Generally the measured wetting efficiencies differ from each other with lower wetting efficiency values, but as the wetting efficiency increases the differences between the prewetting methods diminishes.

7. Conclusions

An improved hydrodynamic model is presented for trickle-bed reactors. The model is based on the hydrodynamic model presented in our earlier work,[1] but modified to take into account partial wetting of the catalyst. In addition, the performance of the model with low liquid velocities, in industrially relevant circumstances and in more complicated, two and three-dimensional situations, was discussed.

Contrary to most published work, comprehensive tests varying the number of dimensionless groups and the dimensionless groups themselves were carried out in the process of the model development. In addition, the wetting efficiency model is not evaluated solely on the wetting efficiency data, but also on its suitability to predict the overall hydrodynamic behavior. Finally its capability to predict correct trends from common experimental observations was considered.

The new hydrodynamic model was also compared to other literature models on the basis of pressure drop, liquid holdup, and wetting efficiency predictions. It was concluded that the new model improved predictions in all areas. In addition, the model is creditably robust to use and convertible to various applications. The model can be used equally well as a tool for design and for modeling of large scale industrial reactors as well as an analysis tool in complicated three-dimensional situations.

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Supporting Information Available: Details of the operation range used in the model development and a more extensive comparison between the hydrodynamic models during the course of model development. This information is available free of charge via the Internet at http://pubs.acs.org.

Appendix

Notation.

a_t = packing external surface area per unit volume of reactor, m^2/m^3
A, B = optimized parameters in eq 12, dimensionless
$B(X)$ = statistical number to test if the model is biased, eq 15, dimensionless
C_i = optimized parameters in eq 13, dimensionless
Ca = capillary number, $Ca = U_L\mu_L/\sigma$, dimensionless
Ca^* = packed bed capillary number, $Ca = U_L\mu_L/\varepsilon\sigma$, dimensionless
d_p = particle diameter, m
E_μ, E_ρ = Ergun constants (180 and 1.8, respectively), dimensionless
$E_{\mu,i}$, $E_{\rho,i}$ = phase specific Ergun constants for phase i (eqs 9 and 10, respectively), dimensionless
$Eö^*$ = Eötvös number, $Eö^* = \rho_L g d_p^2\varepsilon^2/[\sigma(1-\varepsilon)^2]$, dimensionless
$\langle e_X \rangle$ = mean relative error as defined in eq 14, dimensionless
f_e = wetting efficiency, dimensionless
f_τ = friction factor, $f_\tau = E_\rho/(6T_0^3)$, dimensionless
F_{ij} = interaction force between phases i and j, N/m^3
$F_{int,i}$ = total force exerted on phase i, N/m^3
Fr_i = Froude number of phase i, $Fr_i = U_i/\sqrt{g d_p}$, dimensionless
g = gravitational acceleration constant, m/s^2
G_m = superficial gas mass flow rate, $kg/(m^2s)$
Ga_L = liquid Galileo number, $Ga_L = \rho_L^2 g d_p^3/\mu_L^2$, dimensionless
Ga_i^* = modified Galileo number of phase i, $Ga_i^* = \rho_i^2 g d_p^3\varepsilon^3/[\mu_i^2(1-\varepsilon)^3]$, dimensionless
Ka = Kapitza number, $Ka = \sigma^3\rho_L/(\mu_L^4 g)$, dimensionless
L_m= liquid mass flow rate, $kg/(m^2s)$
n = number of dimensionless groups in the wetting efficiency model, eq 13, dimensionless
Oh_L = liquid Ohnesorge number, $Oh_L = \mu_L^2/\sqrt{\sigma d_p \rho_L}$, dimensionless
p = absolute pressure, Pa
$\Delta P/\Delta L$ = pressure drop, Pa/m
Re_L = liquid Reynolds number, $Re_L = \rho_L d_p U_L/\mu_L$, dimensionless
Re_i^* = modified Reynolds number for phase i, $Re_i^* = \rho_i d_p U_i/(\mu_i(1-\varepsilon))$, dimensionless
S_L = liquid saturation, $V_L/\varepsilon V_r$, dimensionless
STD = standard deviation as defined in eq 16, dimensionless
St_i = Stokes number of phase i, $St_i = \mu_i U_i/(\varepsilon\rho_i g d_p^2)$, dimensionless
T_0 = empty bed tortuosity, $T_0 = \sqrt{72/E_\mu}$, dimensionless
T_i = phase specific tortuosity of phase i, eqs 11 and 12, dimensionless
U_i = superficial velocity of phase i, m/s
u_i = interstitial velocity of phase i, m/s
u_r = gas−liquid slip velocity, eq 7, m/s
V_r = volume of the reactor, m^3
We_L = liquid Weber number, $We_L = U_L^2 d_p\rho_L/(\varepsilon^2\sigma)$, dimensionless

Greek Symbols

α = gas saturation, $V_G/\varepsilon V_r$, dimensionless
ε = void fraction of the packed bed, dimensionless
θ_i = volume fraction of phase i, V_i/V_r, dimensionless
$\theta_{L,s}$ = static liquid holdup, $V_{L,s}/V_r$, dimensionless
μ_i = viscosity of phase i, [Pa·s]
ρ_i = density of phase i, kg/m^3
σ = surface tension, N/m
χ = Lochart-Martinelli parameter
$\chi = \sqrt{(\Delta P/\Delta L)_G/(\Delta P/\Delta L)_L}$, dimensionless
$\psi_{\Delta p}$ dimensionless pressure drop, $\psi_{\Delta p} = (\Delta P/\Delta L)/\rho_L g$
Ψ_L liquid phase body force, $\Psi_L = 1 - (\Delta P/\Delta L)/g\rho_L$

Subscripts

G = gas phase
L = liquid phase
LF = liquid full conditions
TP = two phase conditions

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