Monitoring of Itaconic Acid Hydrogenation in a Trickle Bed Reactor Using Fiber-Optic Coupled Near-Infrared Spectroscopy

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Near-infrared (NIR) spectroscopy has been applied to determine the conversion of itaconic acid in the effluent stream of a trickle bed reactor. Hydrogenation of itaconic to methyl succinic acid was carried out, with the trickle bed operating in recycle mode. For the first time, NIR spectra of itaconic and methyl succinic acids in aqueous solution, and aqueous mixtures withdrawn from the reactor over a range of reaction times, have been recorded using a fiber-optic sampling probe. The infrared spectra displayed a clear isolated absorption band at a wavenumber of 6186 cm^{-1} (wavelength 1.617 μm) resulting from the =C–H bonds of itaconic acid, which was found to decrease in intensity with increasing reaction time. The feature could be more clearly observed from plots of the first derivatives of the spectra. A partial least-squares (PLS) model was developed from the spectra of 13 reference samples and was used successfully to calculate the concentration of the two acids in the reactor effluent solution. Itaconic acid conversions of 23–29% were calculated after 360 min of reaction time. The potential of FT-NIR with fiber-optic sampling for remote monitoring of three-phase catalytic reactors and validation of catalytic reactor models is highlighted in the paper.

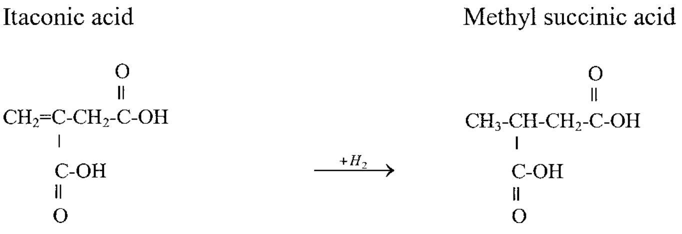
Index Headings: **Near infrared; NIR; Hydrogenation; Itaconic acid; Fiber optics; On-line; Trickle bed reactor; Partial least squares; PLS.**

INTRODUCTION

Catalytic technology plays a major role in the bulk and fine chemical industry.[1] Trickle beds, which consist of fixed beds of catalyst contacted by cocurrent downflows of gas and liquid, are one of the most common types of three-phase catalytic reactors, and their design relies upon models describing reaction kinetics, mass transfer, and hydrodynamics of trickle flow.[2] The primary variables of interest in trickle bed reactor models are the concentration of gaseous reactants dissolved in the liquid and the conversion of liquid-phase reactants.[3] This paper describes the application of fiber-optic coupled near-infrared (NIR) spectroscopy to the monitoring of liquid-phase reactant composition at the outlet of a laboratory trickle bed reactor. It is demonstrated that NIR spectroscopy provides a quick and accurate method of measuring liquid-phase composition and hence conversion of key reactants. The potential of the technique in evaluating models of trickle bed reactors in order to gain confidence in their predictions for catalytic reactor design is identified in the paper.

The use of NIR spectroscopy in remote monitoring has been widely reported in the chemical literature[4,5] and is also being applied to problems of interest to the process industries. For example, Coffey et al.[6] used a fiber-optic coupled acousto-optic tunable filter NIR (AOTF-NIR) to monitor the vapor content of a rotary dryer effluent stream. The method was preferable to analysis by gas chromatography (GC) or Karl Fisher titration, since the need to wait 40 minutes for the results and the possible exposure of process operators to chemical vapor during sampling were avoided. Drying times were more accurately determined by AOTF-NIR, hence avoiding unnecessary drying periods at the end of a batch. Yalvac et al.[7] analyzed a mixture of light alkenes using NIR and Coffey et al.[8] followed a reaction of industrial significance using fiber-optic NIR spectroscopy. Ward et al.[9] used on-line NIR spectroscopy to determine the end point of a bulk pharmaceutical reaction in a closed loop hydrogenator. A palladium/carbon catalyst was used and the reaction solvent was tetrahydrofuran. Monitoring of the process in real time enabled the key reaction to be stopped before the concentration of undesirable by-products reached a critical level.

Itaconic acid hydrogenation has been used as a model reaction in the study of mass transfer and reaction capabilities of multiphase catalytic reactors such as the cocurrent downflow contactor reactor.[10] The reaction between itaconic acid and hydrogen involves the saturation of the C=C double bond as follows:



$$\mathrm{CH_2{=}C(C(=O)OH){-}CH_2{-}C(=O){-}OH} \xrightarrow{+H_2} \mathrm{CH_3{-}CH(C(=O)OH){-}CH_2{-}C(=O){-}OH}$$

The advantages of the above reaction for studying the capabilities of catalytic reactors are that the kinetics are first order with respect to hydrogen, and the reaction can be carried out at low temperatures and pressures of 70 °C and 1.5 bar(a), respectively. In trickle bed reactors, complete consumption of hydrogen cannot be assumed, and therefore the progress of the reaction must be monitored by measuring the concentration of itaconic acid in the liquid effluent from the bed. Traditionally, the concentrations of itaconic acid and methyl succinic acid have been measured using GC. Before injection to the GC, the acids must first be esterified, then extracted in chloroform and dried over anhydrous sodium sulfate.[11] This proce-

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Received 29 August 2002; accepted 4 November 2002.

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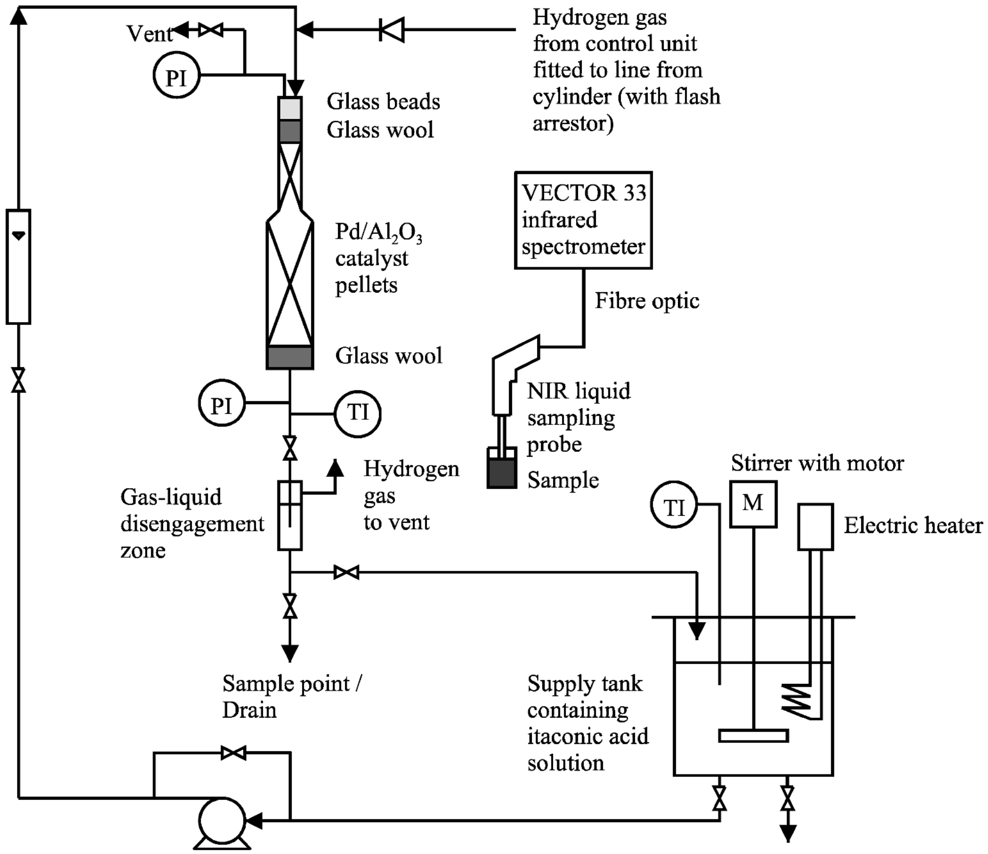

FIG. 1. Experimental setup of the laboratory trickle bed hydrogenation experiment.

dure takes 2–3 h and is subject to experimental errors associated with the esterification and extraction. Therefore, this study examined the application of NIR spectroscopy to the measurement of itaconic and methyl succinic acid concentrations in order to achieve a more accurate measurement in a fraction of the time taken by GC. This paper reports the first known application of NIR to the monitoring of itaconic acid hydrogenation.

In the following section, the experimental setup of the trickle bed hydrogenator and details of the applied infrared spectroscopy techniques are given. The development of a partial least-squares (PLS) model for the calculation of liquid-phase composition from the recorded spectra is described. Then NIR spectra of samples from the reactor effluent stream and plots of the concentrations of itaconic and methyl succinic acids as a function of reaction time are presented and discussed. Finally, the potential of inline NIR for evaluating computer models of trickle bed performance is highlighted.

EXPERIMENTAL

Trickle Bed Reactor Apparatus. A trickle bed reactor rig was constructed as displayed in Fig. 1. The reactor vessel consisted of a glass column 60 cm in depth with a diameter of 5 cm at the top and 7 cm at the base. The feed liquid was supplied to the top of the reactor from a heated tank by a peristaltic pump. Hydrogen gas was also supplied to the top of the reactor, via a non-return valve. The bed was filled with Pd/Al$_2$O$_3$ catalyst pellets 4–8 mm in diameter (Johnson Matthey), packed between glass wool at the top and bottom with a layer of glass beads at the top acting as the distributor. The liquid and gas flow out of the base of the bed and are passed through a disengagement zone; after passing through this zone the liquid was recycled to the supply tank and gas was vented to the atmosphere.

Fourier Transform Near-Infrared System. A VECTOR 33 FT-IR spectrometer (Bruker Optics) was used for the measurements. The instrument was configured for near-infrared operation using a tungsten halogen NIR source, a thermoelectrically cooled InAs detector sensitive over the range 12 800–3470 cm^{-1}, and a NIR quartz beam splitter. A fiber-optic coupling unit was fitted to the right side exit port after the interferometer to focus light onto the fiber-optic cable and direct the return light from the probe to the InAs detector, which was housed in the unit. The probe used was of the quartz immersion type with a fixed 2 mm gap (or path length) and fitted with two single fibers 2 m in length. Spectrometer control and measurements were performed using a Windows NT PC running Bruker OPUS/IR software.

Hydrogenation Experiment with Near-Infrared Monitoring. Prior to carrying out the hydrogenation experiment in the trickle bed reactor, the catalyst was activated by reduction in a flow of hydrogen for one hour. Then, 9.5 L of itaconic acid solution was made up in the supply tank and heated to 60 °C. The hydrogenation experiment then commenced, with liquid feed supplied to the top of the reactor at a rate of 280 mL min^{-1} and hydrogen gas at a rate of 1.5 L min^{-1} (0.002 kg m^{-2} s^{-1})

and 4.2 L min^{-1} (0.005 kg m^{-2} s^{-1}) respectively during two different runs. In the feasibility study reported here, 50 mL liquid samples were taken from the reactor effluent for analysis at 45-min intervals up to a reaction time of 6 h, and NIR spectra of the samples were taken. Measurement conditions were 64 coadded scans with a measurement time of 60.9 s, at a resolution of 4 cm^{-1} (1.1 nm at 6000 cm^{-1}). A background or zero reference spectrum was taken with air.

RESULTS AND DISCUSSION

Calibration. A calibration set was constructed from reference spectra of samples containing known concentrations of itaconic and methyl succinic acids. A set of 13 reference samples and one test sample were prepared by adding the acids in powdered form to water. The concentrations of each acid covered the range 0–0.23 mol L^{-1} across the samples, and the total concentration of the two acids in each sample was 0.23 mol L^{-1}. NIR reference spectra were recorded for each sample by dipping the probe into the sample container. The same experimental measurement parameters were used as for the reactor effluent samples. Each calibration sample measurement was repeated twice with the sample shaken in-between in order to build slight sample-handling variability into the model. Any cross-sample contamination was avoided by cleaning the probe with a tissue between sample measurements.

A PLS calibration model was constructed from the reference spectra using the Bruker OPUS/QUANT software, which is based on the PLS-1 algorithm. In order to make the input spectra more consistent, a data preprocessing of first derivative and vector normalization was applied. The spectral ranges used in the calibration were 6381–5617 cm^{-1} for itaconic acid and 6096–5714 cm^{-1} for methyl succinic acid. These ranges encompass the overtone C–H stretch region of the two acids that remain accessible in between the strong water absorption bands. Figure 2a shows the original 26 absorbance spectra of the calibration samples, which all appear very similar on this scale, whereas Fig. 2b shows the clear differences when the spectral region of interest is expanded considerably after the data preprocessing. Figure 2c highlights the differences between the spectra of pure itaconic and methyl succinic acids in solution after preprocessing.

The quantitative analysis method was checked by cross-validation in the leave-one-sample-out mode (2 spectra left out in turn). Table I shows the concentrations of itaconic, methyl succinic, and total acid for each of the 13 calibration samples determined both gravimetrically and by NIR cross-validation. Figure 3 shows the cross-validation graphs of the actual vs. predicted concentrations of itaconic and methyl succinic acids, respectively. The excellent correlation is indicated by the high R^2 value of 0.9997 for each acid and the low root mean square errors of cross validation (RMSECV) of 0.00120 and 0.00117 for itaconic and methyl succinic acids, respectively. The PLS rank used for both graphs was one.

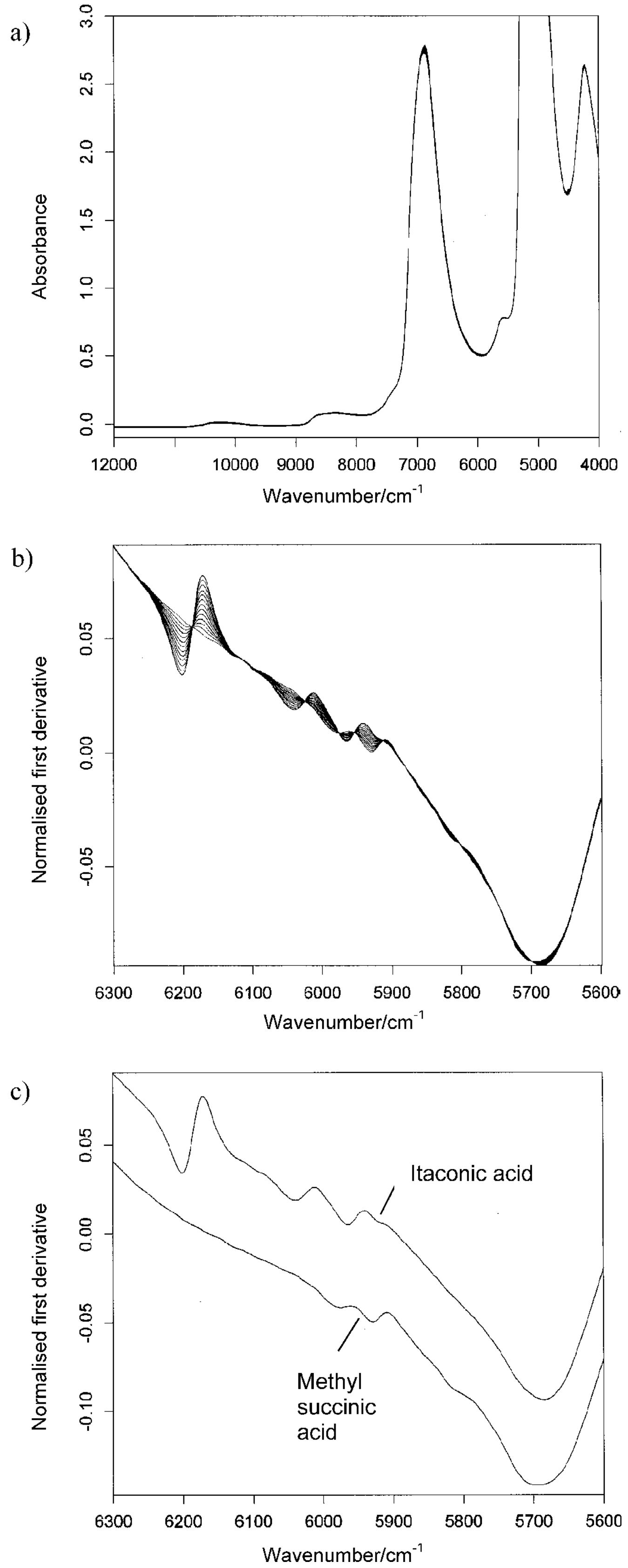

FIG. 2. (**a**) NIR spectra for the calibration samples displayed in the range 12 000–4000 cm^{-1}; (**b**) normalized first-derivative spectra for the calibration samples shown for the range 6300–5600 cm^{-1}; (**c**) normalized first-derivative spectra for pure itaconic acid and methyl succinic acid in aqueous solution over the range 6300–5600 cm^{-1}. The two spectra are offset for clarity.

The RMSECV values are an indication of the accuracy when predicting the concentrations of unknown samples. As a further check, we also measured a test sample, which was prepared gravimetrically (see Table I) and not

TABLE I. Details of the calibration and test samples. Itaconic, methyl succinic, and total acid concentrations determined (1) gravimetrically from the weight of powdered acid used to prepare the sample and (2) from NIR analysis by internal cross-validation for the calibration samples A through M (leave-one-sample-out mode) and by external validation using the final PLS calibration models for the test sample. The data in parentheses represent the difference between measurements (2) and (1).

	Acid concentration determined gravimetrically			Acid concentration determined by NIR; results are averaged for 2 spectra		
Calibration sample	Itaconic acid (mol L^{-1})	Methyl succinic acid (mol L^{-1})	Total acid (mol L^{-1})	Itaconic acid (mol L^{-1})	Methyl succinic acid (mol L^{-1})	Total acid (mol L^{-1})
A	0.2321	0.0000	0.2321	0.2304 (−0.0017)	−0.0004 (−0.0004)	0.2300
B	0.2118	0.0195	0.2313	0.2141 (+0.0023)	0.0181 (−0.0014)	0.2322
C	0.1922	0.0385	0.2307	0.1940 (+0.0018)	0.0378 (−0.0007)	0.2318
D	0.1728	0.0573	0.2301	0.1716 (−0.0012)	0.0595 (+0.0022)	0.2311
E	0.1538	0.0769	0.2307	0.1534 (−0.0004)	0.0780 (+0.0011)	0.2314
F	0.1352	0.0961	0.2313	0.1354 (+0.0002)	0.0967 (+0.0006)	0.2321
G	0.1165	0.1156	0.2321	0.1151 (−0.0014)	0.1151 (−0.0005)	0.2302
H	0.0966	0.1361	0.2327	0.0969 (+0.0003)	0.1347 (−0.0014)	0.2316
I	0.0763	0.1542	0.2305	0.0765 (+0.0002)	0.1550 (+0.0008)	0.2315
J	0.0573	0.1737	0.2310	0.0564 (−0.0009)	0.1731 (−0.0006)	0.2295
K	0.0388	0.1923	0.2311	0.0385 (−0.0003)	0.1928 (+0.0005)	0.2313
L	0.0202	0.2112	0.2314	0.0204 (+0.0002)	0.2125 (+0.0013)	0.2329
M	0.0000	0.2306	0.2306	0.0014 (+0.0014)	0.2289 (−0.0017)	0.2303
Test Sample	0.1659	0.0676	0.2335	0.1661 (+0.0002)	0.0669 (−0.0007)	0.2330

used for calibration. We then took the difference between the predicted concentrations from the calibration model used and the known values from the weight of powdered acids used to prepare the test sample. This cross-check gave actual discrepancies of 0.0002 mol L^{-1} and 0.0007 mol L^{-1} for itaconic and methyl succinic acids, respectively, suggesting that the method is capable of achieving the estimated accuracy of ±0.001 mol L^{-1}.

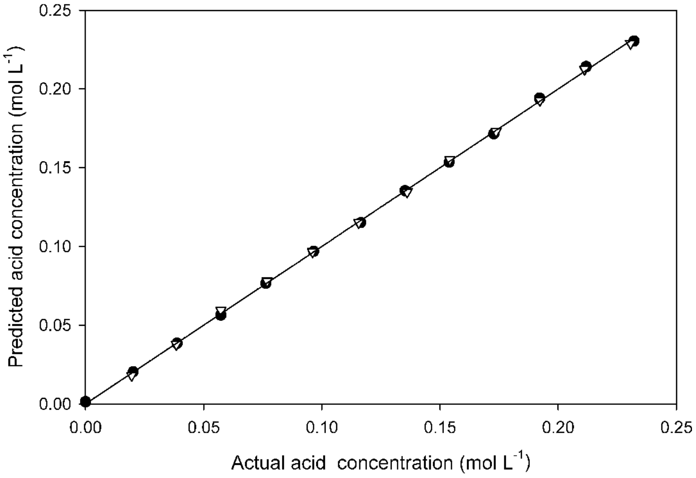

FIG. 3. Cross-validation plots of predicted vs. actual concentrations of itaconic acid (filled circles) and methyl succinic acid (open inverted triangles).

Interpretation of the Spectra. Figure 2a displays the original absorbance spectra of all calibration samples with the main features resulting from water, specifically the 6870 cm^{-1} overtone O–H stretch and the onset of strong absorption below 5500 cm^{-1} due to the O–H stretch-bending combination. It is just possible to see some weak absorption due to the acids in the region of the C–H overtones between 6200 and 5850 cm^{-1} located between these large water peaks. A considerable y-scale expansion of this spectral region after the data preprocessing clearly shows the spectral variations due to the changing acid concentrations, as observed from Fig. 2b. The feature between 6220 and 6160 cm^{-1} is clearly assigned to the vinylic =C–H overtone stretch of itaconic acid, which disappears in pure methyl succinic acid solution, as shown in Fig. 2c. The absorbance decreases as the double bond of itaconic acid becomes saturated during hydrogenation to methyl succinic acid.

Figure 4 shows the raw absorbance spectra of itaconic acid, methyl succinic acid, and four samples taken from the reactor effluent. It is observed that the spectra of the pure samples and reactor effluent are very similar, except in the range 6220–6160 cm^{-1}, where a feature that is sensitive to the extent of reaction occurs. The inset of Fig. 4 shows an enlargement of this feature. The progressive change can be more clearly observed from a plot of the first-derivative spectra, shown in Fig. 5. It is seen that the first-derivative spectra for the reaction mixtures

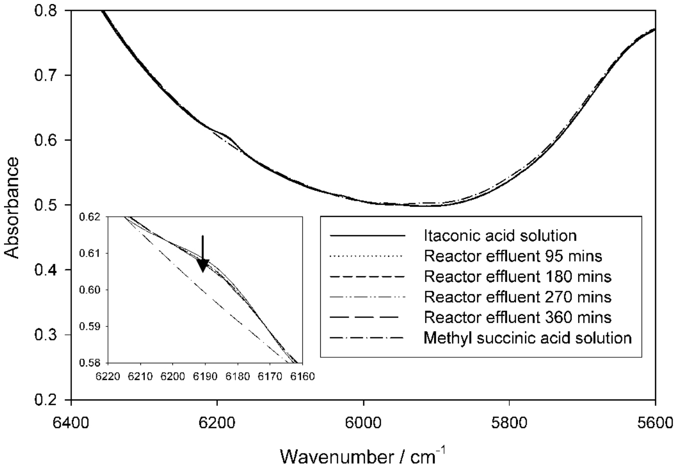

FIG. 4. NIR spectra of itaconic acid solution (0.23 mol L^{-1}), methyl succinic acid solution (0.23 mol L^{-1}), and samples withdrawn from the reactor effluent at various reaction times shown over the range 6400–5600 cm^{-1}. **Inset**: Enlarged figure for the region 6220–6160 cm^{-1} showing a feature that is sensitive to the reactant conversion. The arrow indicates the direction of reaction progression.

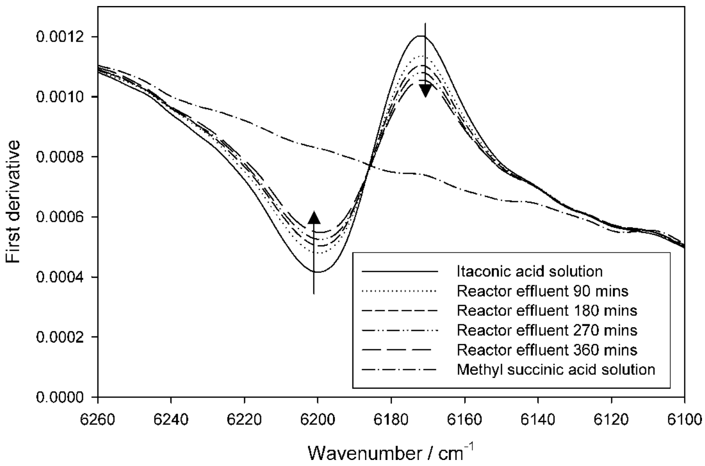

FIG. 5. First-derivative spectra of itaconic acid solution (0.23 mol L^{-1}), methyl succinic acid solution (0.23 mol L^{-1}), and samples withdrawn from the reactor effluent at various reaction times shown over the range 6260–6100 cm^{-1}. Arrows indicate the direction of reaction progress.

gradually approach that of methyl succinic acid with increasing reaction time, indicating a progressive increase in itaconic acid conversion.

Quantitative Analysis. The PLS calibration was used to calculate simultaneously the concentration of itaconic acid and methyl succinic acid for each sample withdrawn from the reactor effluent. In Fig. 6 the concentrations of the two acids are plotted as a function of reaction time for two different hydrogen flow rates through the reactor. The fractional conversion, X, of itaconic acid at time t was calculated from the equation:

$$X = \frac{C_0 - C_t}{C_0}$$

where C_0 is the initial concentration of itaconic acid, and C_t is the concentration at time t. After 360 min of reaction time, the conversion of itaconic acid was 23% and 29% for hydrogen flow rates of 4.2 L min^{-1} and 1.5 L min^{-1}, respectively. The lower conversion at the higher flow rate of hydrogen may have resulted from thinning of the liquid film on the catalysts and associated reduction in liquid hold up at the higher gas flow rate. Also, it is thought that the higher flow rate of hydrogen may lead to a greater temperature decrease over the bed and hence a lower rate of reaction. It is noted that the NIR technique provides scope for in-line reaction monitoring of the reactor effluent stream composition. We will investigate the possible in-line monitoring of reactions in future studies.

Models representing the behavior of trickle bed reactors need to account for the effect of parameters such as liquid hold up, gas–liquid contacting, and catalyst effectiveness upon conversion of reactants in the liquid flowing through the bed. Earlier models of trickle bed reactors assumed plug flow of liquid and used an effectiveness factor to describe the fraction of the external catalyst area wetted by liquid.[12] More recent phenomenological models are based on rigorous analyses of multicomponent mass and energy transfer on the reactor and catalyst scale.[13] Such models will have to be further validated over a wide range of reactor operating conditions in order to gain confidence in their predictions for scaling up reactors. In this paper, it has been shown that NIR spectroscopy with fiber-optic probes can be used to determine the composition of liquid effluent streams from trickle bed reactors and that it is a faster and more accurate analysis method than GC for this application. Since the NIR method used could be easily adapted for in-line analysis, it could be used to evaluate whether the reactor effluent compositions predicted by computer simulations are confirmed by experiments carried out under the same conditions. At Birmingham University, the use of NIR in validating reactor models will form part of on-going studies of three-phase catalytic reactor performance.

CONCLUSION

Near-infrared spectroscopy with a fiber-optic sampling probe has been used to record spectra of itaconic and methyl succinic acids in aqueous effluent solution from a trickle bed hydrogenation reactor operating in recycle mode. A PLS calibration model was constructed from spectra recorded for 13 different reference samples, and cross-validation showed excellent correlation between ac-

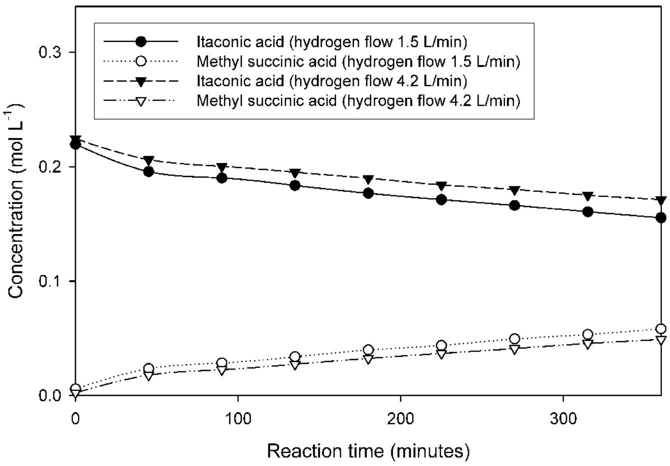

FIG. 6. Concentrations of itaconic and methyl succinic acids in the reactor effluent stream as a function of reaction time at two hydrogen flowrates.

tual and predicted concentrations of the two acids. The PLS model was applied to determine the concentrations of the acids in the reactor effluent stream, and hence, the conversion of itaconic acid was calculated. After a reaction time of 360 min, the conversion of itaconic acid was 23–29%, depending inversely upon the hydrogen flow rate used in the reactor. The potential of the technique for in-line monitoring of three-phase catalytic reactors and verification of trickle bed reactor models was identified.

ACKNOWLEDGMENTS

J. Wood is grateful to Bruker Optics Limited for carrying out the NIR spectroscopic measurements and to Johnson Matthey plc for supplying the catalyst used in the trickle bed reactor without charge.

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