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A MICROREACTOR FOR THE NITRATION OF BENZENE AND TOLUENE

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Narrow channel microreactors have been evaluated for the reaction of immiscible liquid-liquid systems. In order to stimulate rapid interphase mixing and mass transfer, alternating slugs of organic and aqueous phases were generated at a "T" piece and flowed down an etched channel in a glass substrate. The detailed flow behavior was recorded photographically. Finally, some benzene and toluene nitration experiments were performed in stainless steel and PTFE capillary tubing in order to explore the industrial potential of microreactors for chemical production.

***Keywords*:** Capillary; Microreactor; Nitration; Slug flow

INTRODUCTION

Improved methods of manufacturing at microscales have opened up new opportunities for the development of compact, efficient, and highly controllable reactors. Rapid heat and mass transfer between fluids may now be engineered into reactors by the use of small channels for fluid transport. Short path lengths for thermal and molecular diffusion can provide an ideal environment for rapid exothermic/endothermic reactions while maintaining a laminar flow regime. Scale requirements for efficient mixing by diffusion can be characterized using the following equation (Crank, 1975):

$$d = \left(\frac{D.t}{Fo}\right)^{1/2} \tag{1}$$

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where D is the diffusivity of the reacting molecules in the fluid, t the residence time, and Fo the Fourier number that determines the level of mixing. For essentially complete mixing over a distance of d, values of Fo should be close to or greater than unity. Much of the development work in the area of microreactors has focused on the use of narrow channel dimensions for rapid mixing of liquids by pure diffusion. Many references for this work can be found in the *Proceedings of the 4th International Conference on Microreaction Technology* (2000).

Reaction mechanisms involving multiphase flow have been given less attention, partly due to the greater complexity of their behavior in the presence of a fluid interface. Various methods of contacting multiphase flows in a microenvironment have been proposed. One method described by Burns et al. (1997) is to use parallel streams of liquid confined in narrow channels to allow efficient transfer by diffusion across the interface. Devices based on this concept are described by Harper (1997) and Harston et al. (1999). Another method employed for contacting immiscible liquids or liquids and gases is to produce a matrix of fine droplets or bubbles from a structured array of tiny orifices. This method has been most successfully developed by IMM in the form of its Micromixer. Examples of this are given by Zech et al. (2000) and Bayer et al. (2000).

The previously described methods of multiphase contacting do, however, have certain drawbacks. Parallel fluid flow involving purely diffusive transfer requires channel dimensions of below 100 μm to work effectively for rapid reactions. This can lead to high pressure drop requirements or low channel velocities, reducing throughput capabilities for chemical production. Dispersed systems, such as the IMM Micromixer, do allow higher throughput due to the larger pipe diameters, though the small size of the droplets and bubbles can create an additional postreaction separation requirement.

A third method of contacting immiscible liquids was sought that would allow greater throughput per channel and easy separation; this has lead to the consideration of slug flow as a means of liquid contacting. Slugs of liquid, when confined within narrow channels, can be used to generate high frequency internal circulation due to the combination of shear within the channel and interfacial phenomena. Internal circulation generated by interfacial shear across a droplet interface has long been known as a method of enhancing mass transfer and is described in a wide range of literature, such as Clift et al. (1978). Typical circulation frequencies of 10–100 Hz may be expected in submillimeter slugs traveling velocities of the order of cm per second. This provides a method of rapid transport to and from the interface, increasing the concentration gradients and mass transfer performance. Slug lengths are generally longer than the channel width with volumes equivalent to droplets with diameters two or three times the channel width. Separation of the phases at

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the end of the reactor channel, with a reasonable density difference, may therefore in many cases be achieved through buoyancy due to relatively large slug volumes compared with emulsified systems.

The use of slug flow inside a microreactor for the nitration of benzene and toluene forms the basis of the experimental work described here.

EXPERIMENTAL FACILITY

An experimental investigation of multiphase flow through narrow submillimeter channels was conducted in a range of devices and materials. Initial work in this area was performed in etched stainless steel and glass systems and has been described in earlier publications by Burns et al. (1997). The development of devices to generate slug flow for reactions concentrated on the use of transparent materials, such as glass and perspex, that allowed easy visualization of the flow patterns. The simplest mechanism for generating slug flow was the use of a T-junction with three intersecting channels. Figure 1 shows an example of a typical device constructed in glass using a slitting saw to cut the 380 μm wide and deep channels. Slug lengths of around 1.6 mm were generated in this device using a mixture of silicon oil and kerosene (dyed dark blue) for the organic phase and water for the aqueous phase.

Figure 2 illustrates the circulation patterns theoretically expected to form inside the slugs due to the combination of the fluid interface and the shearing flow along the narrow channel. Circulation times within the slugs can be characterized by the ratio of the slug length L and average slug velocity v so that

$$\text{Circulation Time} \approx \frac{2L}{v} \tag{2}$$

For the slugs illustrated in Figure 1 with a length of 1.6 mm traveling at a relatively slow velocity of 5.6 mm.s^{-1}, this would give a characteristic circulation time of 0.6 s. However, in the capillary reactor system described in the following experimental work, liquid velocities of several

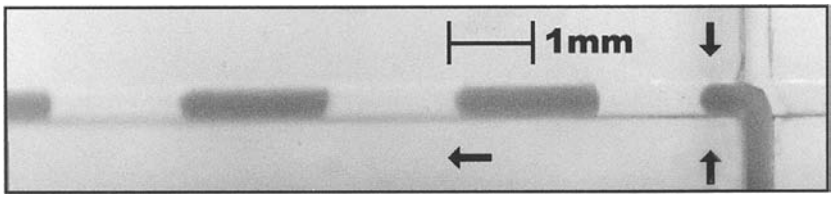

Figure 1. Photograph of slug flow generation in a glass channel. Channel width and depth approximately 380 μm, organic phase contained a dark dye.

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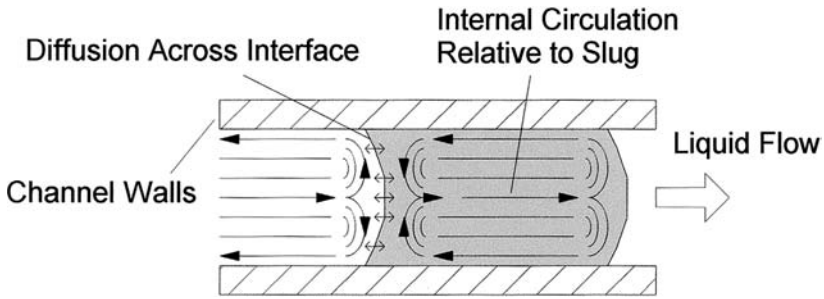

Figure 2. Illustration of circulation patterns generated inside each liquid slug.

cm.s^{-1} with slugs of typically 0.5 mm to 0.6 mm length provide much faster circulation times in the region of 0.02 s.

A more flexible design was adopted for the nitration process in which narrow-bore capillary tubes were used to provide the reactor channels. The use of capillary tubes allowed easy variation in channel length and diameter. Both PTFE and stainless steel systems were produced using a range of narrow-bore capillary tubes that provided the environment for liquid mixing. Figure 3 shows the experimental facility used for performing the reaction work.

Organic and aqueous flow was supplied either continuously from HPLC pumps or from syringe drivers. These were connected to feed capillaries of 254 μm bore for stainless steel systems and 300 μm bore for PTFE systems. All capillary tubes used for the system were 1.59 mm outer diameter. The feed capillaries transported the liquids from the pumps to the distributor illustrated in Figure 4. Early distributors were produced in stainless steel and later versions were made in PTFE as shown in Figure 4. The distributor consisted of channels drilled out to the same diameter as the capillary tube so that it could be fully inserted, thereby giving the minimum internal liquid volume. However, a small gap was left when positioning the tubes to allow liquid transfer into the

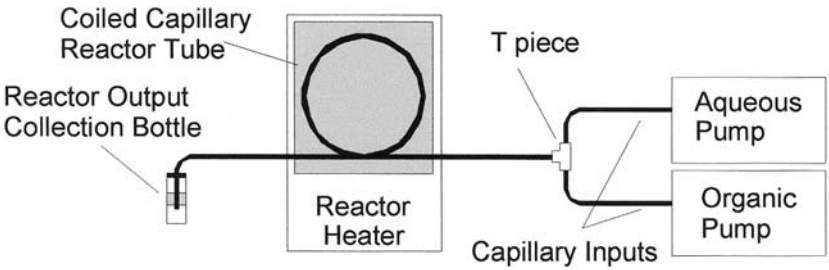

Figure 3. Layout of capillary reactor used for organic nitration.

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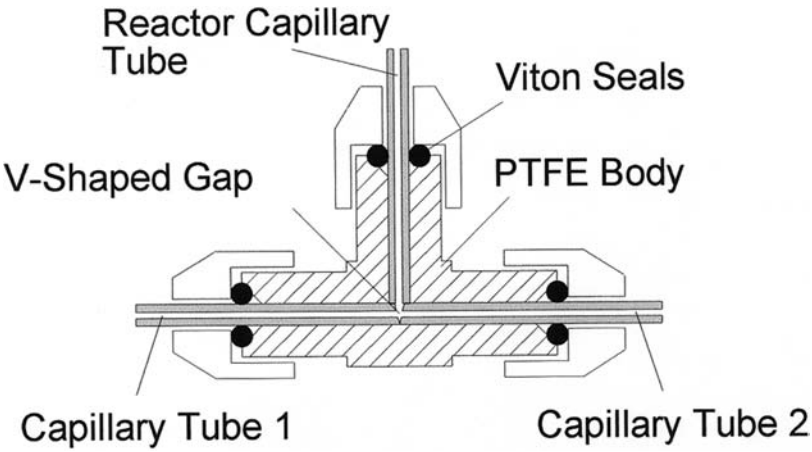

Figure 4. PTFE T piece used for the capillary reactor.

reactor capillary. Experiments with several designs of liquid distributor have been described earlier by Burns and Ramshaw (1998). These suggested that the minimization of internal volume was crucial for ensuring the production of short slug lengths in the reactor flow.

A capillary tube of length between 30 cm and 180 cm was used to perform the nitration with internal diameters in the range of 127 μm to 300 μm. This length of tube was chosen to allow several $cm.s^{-1}$ flow velocities with rapid internal circulation while maintaining acceptable pressure drops of the order of a few bar. The reactor tube was coiled and placed on a hot plate that was insulated with layers of polyurethane foam along with thermocouples to verify tube temperature. Due to the rapid heat transfer into the narrow channel coupled with low liquid volumes the reaction was performed effectively isothermally at the tube temperature measured by the thermocouples.

Slug generation within the PTFE capillary reactor could be checked visually using a stroboscope. Photographs of flow within the capillary were also taken for a nonreacting system using a dyed organic phase. Figure 5 shows the slug flow pattern within a 150 μm bore PTFE capillary

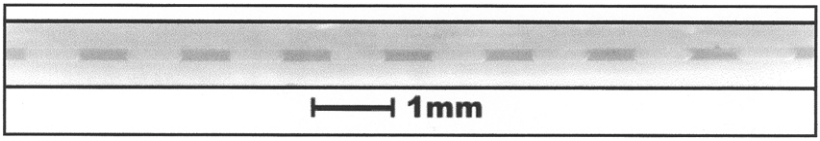

Figure 5. Slug flow generated inside a 150 μm bore PTFE capillary tube. Organic phase colored with a dark dye.

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tube using the distributor shown in Figure 4. Slug lengths of 0.5 mm to 0.6 mm were typically generated using this mechanism.

MIXED ACID NITRATION WITHIN THE CAPILLARY REACTOR

The mechanism of mixed acid nitration is a well-established process for the production of nitrated aromatics whose details can be found in a wide range of texts (Schofield, 1980; Albright and Hanson, 1975). Various examples of industrial processes using this method of nitration may be found, such as those described by Alexanderson et al. (1978) and Guenkel et al. (1994).

Mixed acid nitration is both highly exothermic and mass transfer limited with performance relying strongly on good heat and mass transfer. The basic mechanism uses H_2SO_4 to catalyze the generation of NO_2^+ ions from HNO_3. These attack organic molecules passing across the interface into the aqueous phase, producing nitrated product that diffuses back into the organic phase. Poor mixing in this process reduces reaction rates and leads to a buildup of dissolved nitrated product near the interface, which can be further nitrated to form often unwanted di-nitro and tri-nitro compounds. Oxidation of the aromatic due to the action of the HNO_3 is also a common problem leading to unwanted byproducts such as phenols and picric acid in the nitration of benzene and cresols in the nitration of toluene.

Mixed acid nitration was performed inside the capillary reactor using a range of acid mixtures, temperatures, flow rates, and organic/aqueous flow ratios. Analysis of the output was performed using gas chromatography to determine the ratios of organic products. Output from the reactor was collected in a sample bottle containing aqueous and organic solvents. These were mostly toluene and water for benzene nitration and dichloromethane for toluene nitration. A few mL of solvent were used, which diluted and cooled the output and effectively quenched the reaction.

Reaction rates for the mono-nitration process were calculated using an interfacial nitration model aimed at fast reaction regimes. This model assumes that organic nitration occurs in the aqueous phase close to the interface and is controlled by mass transfer of organic across the interface and the kinetics within the acid phase. Analysis of the reaction generally focuses on the consumption of nitric acid rather than the production of a particular product. This provides a better method of comparison between reactions where both di-nitro and mono-nitro products may be formed. Models for organic nitration have been provided in various publications (Schofield, 1980; Albright and Hanson, 1975) with variations depending upon the mass transfer and kinetic limitations of the process. The closest model to that of the fast diffusion limited regime assumed to operate

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within the capillary was provided by Schofield, based on the work of Dankwerts (1970). This model may be written as:

$$\frac{d[HNO_3]}{dt} = -a.\left([ArH]_S.\frac{[ArH]}{[ArH]_{t=0}}\right).\sqrt{D.k_2.[HNO_3]} \tag{3}$$

where "a" is the interfacial area per unit volume of acid and $[ArH]_S$ the solubility of the organic within the acid phase. The term on the far right of Equation (3) represents the reaction with the boundary layer close to the interface where the nitration occurs. The volume of this zone and the rate of nitration within it is governed by the diffusion of chemicals into the zone, given by the diffusion coefficient D, and the kinetics of the reaction, given by the rate constant k_2, which is a strong function of H_2SO_4 concentration. Equation (3) also serves to illustrate the equal importance of both kinetics and mass transfer on the observed reaction rate. Simplification of Equation (3) may be achieved by representing nitric acid and organic concentrations as proportions of their initial values using the following equations:

$$X = \frac{[HNO_3]}{[HNO_3]_{t=0}} \quad \text{and} \quad Y = \frac{[ArH]}{[ArH]_{t=0}} \tag{4}$$

For the simple case of mono-nitration, which is the bulk process in the majority of experiments, mass balance implies that equal numbers of organic and nitric molecules are consumed and therefore,

$$\frac{dY}{dt} = \frac{[HNO_3]_{t=0}}{[ArH]_{t=0}}\frac{dX}{dt} \quad \text{and} \quad Y = 1 - \frac{[HNO_3]_{t=0}}{[ArH]_{t=0}}(1-X) \tag{5}$$

Combining Equations (3), (4), and (5) yields:

$$\frac{dX}{dt} = -a.X^{1/2}\left[1 - \frac{[HNO_3]_{t=0}}{[ArH]_{t=0}}(1-X)\right]\sqrt{\frac{D.k_2.[ArH]_S^2}{[HNO_3]_{t=0}}} \tag{6}$$

Equation (6) shows that the rate of consumption of nitric acid should depend upon the kinetics of the acid mixture, the mass transfer rate between phases, and the organic and nitric acid concentrations within the reactor. When the organic and nitric acid concentrations are similar then $[HNO_3]_{t=0} \approx [ArH]_{t=0}$ and $X \approx Y$. Equation (6) can then be approximated to the following form:

$$\frac{dX}{dt} = -RX^{3/2} \tag{7}$$

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where R is a general rate constant for the reaction that is a function of mass transfer and kinetic rates. Integration of Equation (7) allows the following calculation of the constant R from the proportion of nitric acid remaining at time t:

$$R = \frac{2\left(X^{-1/2} - 1\right)}{t} \tag{8}$$

The value of R may also be described as the "initial reaction rate" as it is equal to the theoretical reaction rate at the start of the reaction as shown by

$$R = -\left.\frac{dX}{dt}\right|_{t=0} \quad \text{since} \quad X = 1 \text{ at } t = 0 \tag{9}$$

The use of Equation (6) for the slug flow environment within the microreactor was limited to its theoretical description of the order of the reaction. Since the process described within the model assumes mass transfer only by diffusion, the contributions of convection were not accounted for, and as such Equation (6) has no link to slug geometry or flow velocity. More general empirical models were therefore used to link the calculated reaction rate, given by Equation (8), to the operating conditions of the reactor.

Results: Benzene Nitration Using a Stainless Steel Reactor

Initial experimental work concentrated on benzene nitration and used a stainless steel capillary reactor with 127 μm, 178 μm, and 254 μm bores. Various acid strengths and reactor temperatures were used in the nitration work and comparisons were made of the reaction rate and byproduct formation. A syringe driver was used to supply the flow for the experiments. A 1 mL glass syringe was used to supply acid to the reactor and a 100 μL plastic syringe was used to supply benzene. This resulted in an acid/organic flow ratio of 10.5 for all experiments.

Relatively low concentrations of nitric acid were used for the process to provide a benzene/nitric mole ratio in the region of 0.8 to 1.8. The flow ratio was chosen to provide a reaction regime similar to other benzene nitration studies, such as those described by Alexanderson et al. (1978) and Guenkel et al. (1994).

The first experiments performed were aimed at examining the influence of capillary diameter on the performance of the reactor. Two 50 cm long stainless steel tubes with internal diameters of 127 μm and 254 μm were used to perform the reaction. A relatively high concentration of H_2SO_4 was used in the acid batch to provide a strongly mixing limited

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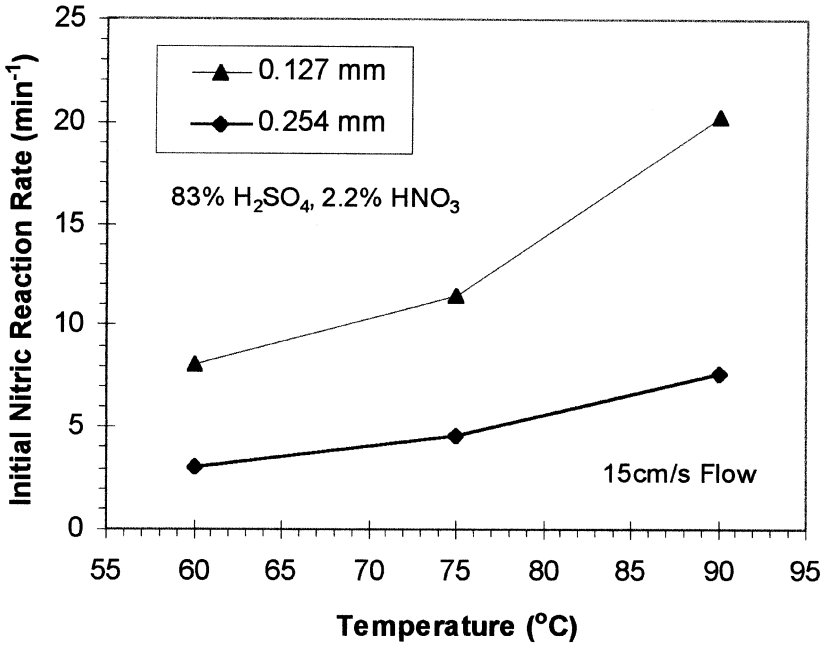

Figure 6. Reaction rates for benzene nitration assuming a shell nitration model. (Experiments conducted with 83% H_2SO_4 and 2.2% HNO_3.)

regime. Averaged results for three different reactor temperatures are shown in Figure 6 with flow velocities of $15\,cm.s^{-1}$ in all cases. These show a clear enhancement in nitration rate when the narrower bore tube was used for the reaction. An average rate enhancement of 2.6 times was indicated in this experiment for the 127 μm bore compared with the 254 μm bore.

Examination of the influence of velocity on reaction rates was also undertaken using several acid batches with 70% to 85% H_2SO_4. The averaged nitric acid reaction rates obtained are shown in Figure 7. As expected increased concentrations of H_2SO_4 yielded faster reaction rates due to increased production of NO_2^+ ions. However, increased velocity also led to faster reaction rates, especially for higher H_2SO_4 concentrations where the reaction should be more mass transfer limited. An exponential relationship between rate constant R and flow velocity v of the form shown in Equation (10) was found to fit the results best. Values of empirical constants R_V and b based on the data provided in Figure 7 are listed in Table I.

$$R = R_V.\exp(b.v) \tag{10}$$

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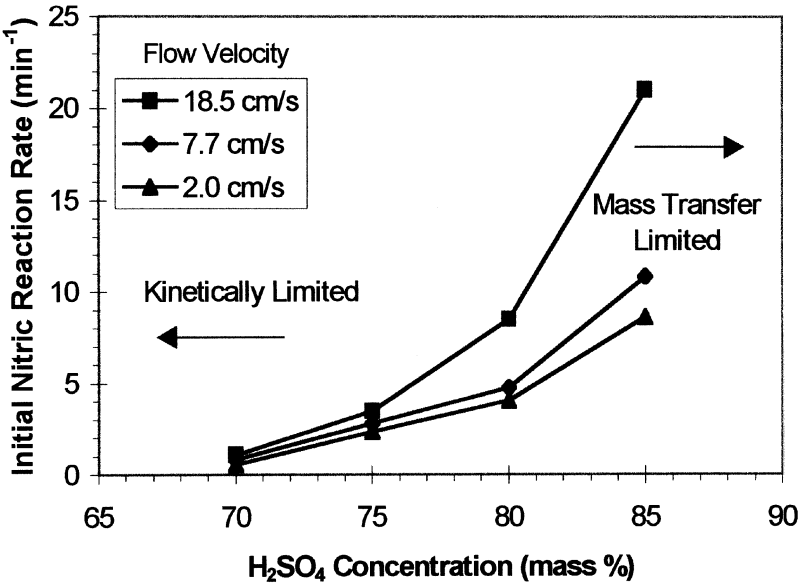

Figure 7. Reaction rates for benzene nitration at different flow velocities. (Experiments conducted with 178 μm bore reactor at 90°C with 4% HNO_3.)

A comparison of the quantity of nitrated product created in the reactor for various reactor lengths was also performed. This was used to confirm that the nitration was taking place mainly within the capillary rather than at some point upstream or downstream. Three reactor lengths of 61 cm, 122 cm, and 183 cm were used for the experiments with three different medium-strength acid batches. A velocity of 7.6 cm.s^{-1} was used in all of the experiments. The results are shown in Figure 8 with the percentage of nitrobenzene, by mass, in the output organic given for the three tubes. The results show a general rise in nitrobenzene concentration as tube length and residence time were increased, confirming that nitration was occurring within the capillary tube. A simple model for the consumption of benzene based on this data was difficult to establish, with no clear order of reaction fitting all of the results.

Table I Empirical Constants for Eq. (6) Based on Data Shown in Figure 7

H_2SO_4	70%	75%	80%	85%
R_V (min^{-1})	0.57	2.28	3.55	7.45
b (cm^{-1}.s)	0.0367	0.0234	0.0461	0.0551

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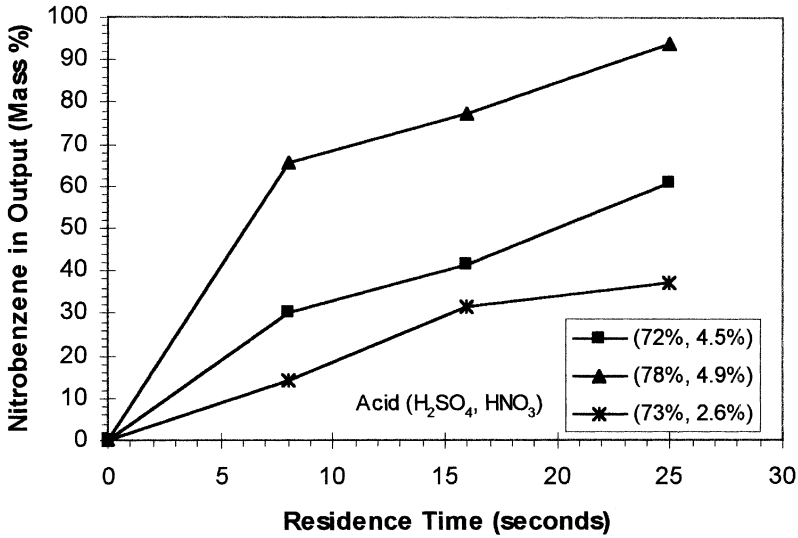

Figure 8. Concentration of nitrobenzene in output organic for three acid batches. (178 μm bore tubing of 61 cm, 122 cm, and 183 cm lengths used at 90°C.)

Toluene Nitration Using a PTFE Reactor

More recent work used PTFE for the construction of the capillary reactor. This has several advantages over stainless steel such as high corrosion resistance and ease of cutting and machining. The low surface energy of PTFE was also expected to encourage interface detachment and slug formation, based on previous flow visualization data.

Toluene nitration was performed with 150 μm bore tubing using a range of acid strengths, reactor temperatures, and flow ratios. A continuous process was operated using HPLC pumps for several of the experiments, allowing easy manipulation of the flow ratios and longer run times. However, corrosion problems with these pumps limited their lifetime for this process.

Initial studies of toluene nitration concentrated on the examination of temperature and flow ratio on reaction rates for an acid mixture similar to that used for benzene nitration. This was composed of 78% H_2SO_4 and 7% HNO_3. Reaction rates were calculated as for the benzene nitration using the consumption of nitric acid to characterize the process. The results showed a significant level of dinitrotoluene formation, compared with the limited dinitrobenzene formation in the benzene process, and this was accounted for in the calculation of nitric acid consumption.

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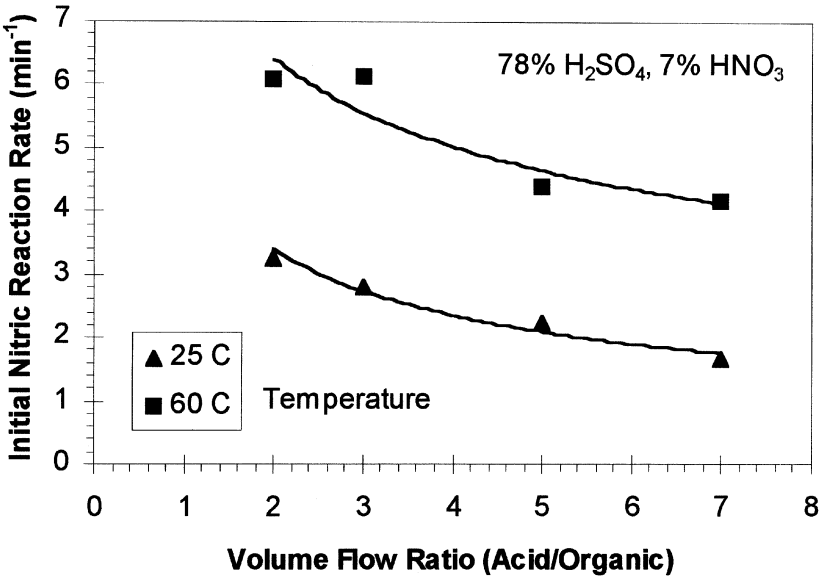

Figure 9. Nitric acid reaction rates for toluene nitration in a 150 μm PTFE reactor. (Experiments used 78% H_2SO_4 with 7% HNO_3.)

Figure 9 shows the nitric acid reaction rates for acid/organic flow ratios of between 2 and 7 at 25°C and 60°C. The results show as expected that reaction rates increase with temperature. The results also show a decrease in nitric acid reaction rate as the proportion of acid used in the reactor was increased. This was expected from Equation (6) due to the lower proportion of organic available within the reactor for the nitric acid to react with. However, a greater organic conversion was achieved when using higher proportions of acid.

Toluene nitration was later examined over a wide range of H_2SO_4 and HNO_3 concentrations. Figure 10 shows the level of toluene conversion obtained using three different acid mixtures. A 135 cm long capillary reactor operating at room temperature was used with a flow velocity of 11.3 cm.s^{-1} and residence time of 12 s throughout these experiments. For the medium and high H_2SO_4 concentrations of 63% and 80% conversion to nitrotoluene and dinitrotoluene was continually enhanced as the acid/organic ratio was increased. For the lower H_2SO_4 concentration of 49%, however, this effect was reduced, and little improvement in organic conversion was gained when using acid/organic flow ratios greater than 2.

The influence of flow velocity on reaction rates was also strong for toluene nitration. Results from experiments using a range of flow velocities are shown in Figure 11. In this case a simple power law

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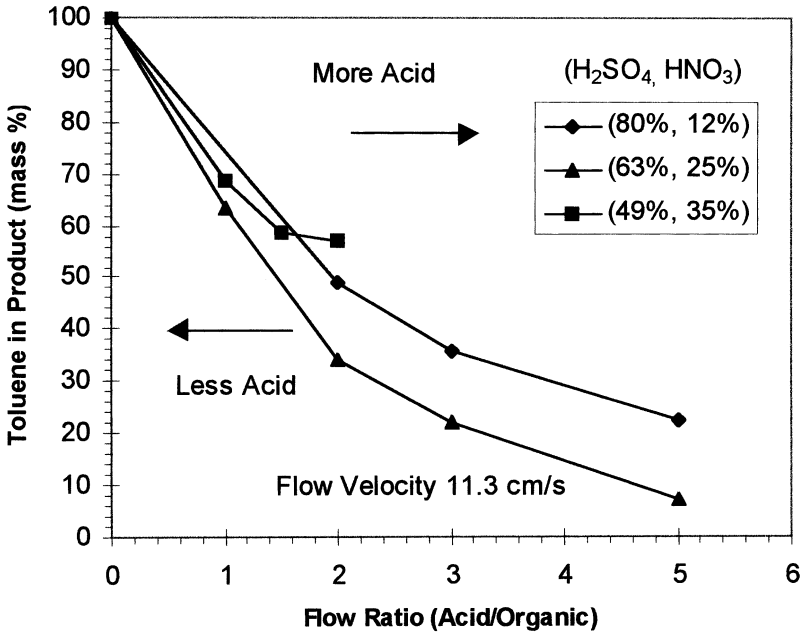

Figure 10. Toluene conversion for a range of acid/organic flow ratios. (All experiments conducted at room temperature.)

relationship, as shown in Equation (11), appeared to fit the data best, with the rate enhanced most significantly for a strong H_2SO_4 concentration with faster kinetics. Best fit values for the exponent m based on the data in Figure 11 are shown in Table II.

$$R \propto v^m \tag{11}$$

Dinitrobenzene and Dinitrotoluene Production

For benzene nitration, the levels of dinitrobenzene production were generally in the region of 1,000 ppm to 10,000 ppm for most experiments. This proportion increased strongly as more H_2SO_4 was used in the acid, with several percent production when 85% H_2SO_4 was used. Temperature, however, had a lesser influence on dinitrobenzene levels, with only marginal increases in its concentration when higher reaction temperatures were used.

Toluene nitration as performed in the PTFE reactor experiments did produce more dinitro product than benzene nitration. As with benzene nitration, levels of H_2SO_4 had the most significant influence on DNT (dinitrotoluene) production. Typical ratios of DNT to NT (nitrotoluene)

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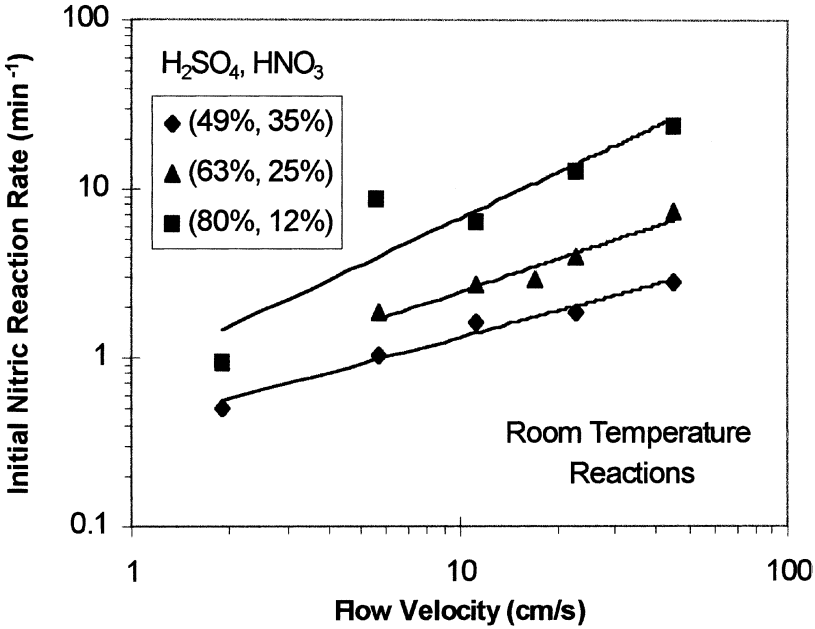

Figure 11. Reaction rates for toluene nitration in at various flow velocities. (Acid/Organic flow ratio of 1:1 for all reactions.)

from the experiments shown in Figure 10 are provided in Table III. The influence of H_2SO_4 is most likely due to increased NO_2^+ production and more rapid consumption of toluene at the interface, shifting the ratio of dissolved NT and toluene in the acid and hence the relative reaction rates.

Oxidation Byproducts

Analysis of oxidation byproducts was limited to the nitration of benzene where phenol groups were produced. High-sensitivity gas chromatography was used to detect nitrophenol, dinitrophenol, and picric acid within the organic output of the benzene nitration. Limits of detection for nitrophenol and dinitrophenol were 10 ppm and for the less stable picric acid 100 ppm.

Table II Empirical Constants for Eq. (7) Based on Data Shown in Figure 11

H_2SO_4	49%	63%	80%
m	0.52	0.65	0.92

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Table III Average Ratio of DNT to NT in Output from Experiments Shown in Figure 10

H_2SO_4	49%	63%	80%
DNT/NT	0.04	0.14	0.58

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Results in general showed lower levels of phenols within the output than those typical of the industrial process, with levels of dinitrophenol being generally much lower in concentration than dinitrobenzene in the output. Experiments performed using 78% H_2SO_4 with 4.5% HNO_3 showed dinitrophenol levels of between 200 ppm to 1100 ppm, and nitrophenol levels between 40 ppm to 2000 ppm when temperature was increased from 80°C to 120°C. No picric acid was detected in any experiments, suggesting levels below 100 ppm in the output.

In general, temperature was observed to have a strong effect on the level of phenol-based byproducts, with levels of below 1200 ppm of oxidized byproducts for 80°C experiments. Experiments using weaker H_2SO_4 concentrations had lower byproduct levels, or none detected, but were difficult to quantify accurately.

DISCUSSION AND CONCLUSIONS

Results have shown that slug flow within the capillary reactor can be used to provide an efficient means of mass transfer between two immiscible reacting liquids over time scales measured in seconds. For both benzene and toluene nitration the results have shown that higher flow velocities can be used to enhance reaction rates, at the cost of increased pressure drops, probably due to the increased convective transport within the slugs. The exact numerical role of velocity on general performance of the reactor was less clear, as can be seen through the differences in the empirical models shown in Equations (10) and (11). This may partly be due to differences in the chemical systems used for the nitrations, but ultimately underlines the need for fluidic modeling of mass transfer behavior of slug flow at this scale.

A positive effect may also be seen in the reduction of the capillary diameter, which should provide shorter path lengths for molecular diffusion. Clearly some trade-off between performance and pressure drop is required for system optimization, but the results emphasize that short path lengths for diffusion combined with rapid internal circulation lead to improved reaction rates within the capillary reactor.

Results from both benzene and toluene nitration have indicated that reaction rates in the range of $0.5\,\text{min}^{-1}$ to $20\,\text{min}^{-1}$ can typically be

Table IV Comparison of Benzene Nitration Performance in the Capillary Reactor with Some Existing Patented Processes

Information Source	Inlet (°C)	Outlet (°C)	H_2SO_4 (mass%)	NB (mass%)	DNB (ppm)	DNP (ppm)	Time (s)	Rate (min^{-1})
Alexanderson	80	128	60.6	89.5	Below 100	1000	120	0.9
Alexanderson	80	134	65.2	99.1	290	1800	120	2.1
Guenkel	95	120	69.5	90	50	1700	25	4.6
Capillary 178 μm	90	90	77.7	94.0	4000	350	24.4	5.9
Capillary 178 μm	90	90	72.2	60.7	Below 1000	Below 100	26.1	1.6

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produced from a capillary reactor. A comparison of benzene nitration results with some existing processes is given in Table IV. The reaction rates shown for the benzene nitration in the capillary reactor in Table IV were taken from results showing levels of byproducts similar to industrial processes. Higher reaction rates could be achieved using the capillary reactor at the expense of increased levels of dinitrobenzene and dinitrotoluene.

Acid composition has been shown to have a strong influence on reactor performance for both benzene and toluene nitration. In both cases greater concentrations of H_2SO_4 have lead to faster reaction kinetics, giving more rapid nitration but also higher levels of dinitro compounds in the output. Flow ratio has also been seen in the case of toluene nitration to influence the reaction within the capillary with nitrobenzene and nitrotoluene yields increasing when more acid is used in the reactor. The influence of extreme flow ratios on slug length and mass transfer is as yet unclear, and more work will be required in studying the fluid dynamics of the slug flow in order to optimize flow ratio and chemical composition for the reactor.

Levels of oxidation byproducts such as nitrophenol and dinitrophenol appear to be significantly less than those reported in other processes when lower reactor temperatures are used. This may be partly due to differences in acid composition and the isothermal nature of the reactor. It may also be due to fundamental differences in the method of contacting the phases. It should be noted that no significant attempt has been made to optimize the capillary reactor chemistry or operation towards achieving lower byproducts, so it may be expected that improved product quality should be achieved from a fully optimized process.

Throughout these experiments the total throughput from the capillary reactor has been of the order of $1\,\mu l.s^{-1}$. Scaling of the reactor is clearly essential if it is to be used to produce significant quantities of product. Methods of scaling will depend strongly on the process requirements. For kgs to tonnes per year 1 to 100 capillaries would

suffice, which may be created by simple manifolding methods. For larger outputs, etched microreactors containing thousands of channels working in parallel will be necessary. Work is underway to develop etched systems to perform these reactions using stacked sheets containing many etched capillary reactors, and this will be reported in future publications.

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NOMENCLATURE

a	interfacial area per unit volume of acid, m^{-1}
b	constant in rate Equation (7), $m^{-1}.s$
D	diffusivity, $m^2.s^{-1}$
d	path length for diffusion, m
Fo	Fourier number
k_2	second order rate constant, $litre.mole^{-1}.s^{-1}$
L	length of slug, m
m	exponent of velocity
R	general rate constant, s^{-1}
R_V	reaction rate constant for zero velocity, s^{-1}
t	residence time, s
v	average flow velocity through channel, $m.s^{-1}$
X	proportion of nitric acid remaining
Y	proportion of organic that has not been nitrated
$[ArH]_S$	solubility of organic phase in acid, $mole.litre^{-1}$
$[HNO_3]$	concentration of HNO_3 in acid, $mole.litre^{-1}$

Abbreviations

DNB	dinitrobenzene
DNP	dinitrophenol
DNT	dinitrotoluene
NB	nitrobenzene
NT	nitrotoluene
PTFE	poly-tetra-fluoro-ethylene

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