



## The mesoscale oscillatory baffled reactor facilitates intensified kinetics screening when the solvent is removed

J.R. McDonough\*, A.N. Phan, A.P. Harvey

School of Engineering, Merz Court, Newcastle University, Newcastle upon Tyne, NE1 7RU, UK



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### ABSTRACT

There are numerous potential benefits of conducting chemical reactions in the absence of solvent. For instance, the risk of environmental release of the solvent is eliminated and there is the potential for intensification via increased reaction rates reducing the required reactor volume. It was previously shown that two configurations of the mesoscale oscillatory baffled reactor (heat pipe and jacketed) could address the challenge of performing exothermic reactions without a solvent, by removing or spreading out the heat released. This could lead to a new approach in green chemistry. Here, this concept was extended to reaction kinetics screening from the same exothermic imination reaction conducted without a solvent. The effects of up to three operating variables (residence time, reactant molar ratio and temperature) were screened in a single flow experiment. It was found that both reactor configurations were able to obtain the Arrhenius kinetic parameters: activation energies of  $103.98 \pm 3.79$  kJ/mol and  $98.11 \pm 1.55$  kJ/mol, respectively, for the two imine synthesis steps. This demonstrated that meaningful data could be obtained, even though the solventless reaction medium was changing as a function of the reaction. Other benefits of this green chemistry approach include: high reaction rates/throughputs, reduced preparation time and reduced downstream purification requirements.

### 1. Introduction

Solvents are substances/mixtures that can dissolve single or multiple solutes to produce homogeneous solutions [1]. Two of the primary functions of solvents are to reduce mass transfer limitations by providing a homogeneous reaction medium, and act as heat sinks for exothermic reactions or heat distribution mediums for endothermic processes. Other uses include reaction rate/mechanism modification, product recovery (e.g. recrystallization) and spectroscopic detection/analysis (e.g. increasing the volume of micro-samples).

However, excessive solvent use can have environmental and economic consequences. For instance, the E factors (defined as kg waste/kg product) for processes involving solvents range from 1 to 5 for bulk chemicals ( $10^4$ – $10^6$  tons of product) to as high as 25–100 for pharmaceuticals ( $10$ – $10^3$  tons of product) [2]. Additionally, solvents must be removed from the final product, usually by evaporative methods such as distillation. As well as creating additional downstream cost/complexity, the recovery of the solvent is typically only in the range of 50–80% [2]. Therefore, there are increasing drivers for the adoption of ‘green solvents’ to improve sustainability by reducing waste and minimising release to the environment. The four conventional green solvent approaches are: (i) substitution (replacing hazardous/toxic

compounds), (ii) bio-solvents derived from renewable sources, (iii) supercritical fluids (typically supercritical water or carbon dioxide), and (iv) ionic liquids with very low vapour pressures [3]. However, the ideal “solvent” would be no solvent at all. Drivers for a no-solvent approach are presented in the following list. Clearly, these potential benefits are additive: intensification is achieved simultaneously through reduced equipment size, eliminated unit operations and reduced energy consumption.

- Elimination of the risk of release of environmentally active solvents
- Removal/minimisation of the requirement for downstream purification
- Intensification of the reactor volume by reducing the total reaction media volume
- Potential reaction rate enhancement through the removal of dilution effects and operation at elevated temperatures (for exothermic processes), further minimising the required reactor volume
- Reduction of the heating/cooling duties because of the smaller thermal mass of reaction media (i.e. reduced handling costs/complexity)

However, there are limitations to the adoption of a no solvent (and

\* Corresponding author.

E-mail address: [jonathan.mcdonough@ncl.ac.uk](mailto:jonathan.mcdonough@ncl.ac.uk) (J.R. McDonough).

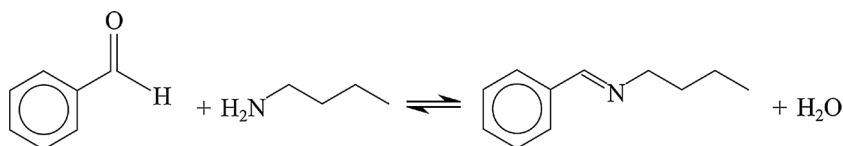
Nomenclature			
$A_i'$	Arrhenius pre-exponential factor for reaction $i$ ( $i = 1, 2$ ) ( $\text{L.s.mol}^{-1}$ )	$T_j$	Jacket temperature (K)
$A(\omega_n)$	Absorbance at wavelength $\omega_n$	$V$	Volume ( $\text{m}^3$ )
$E_{a,i}$	Activation energy for reaction $i$ ( $i = 1, 2$ ) ( $\text{J.mol}^{-1}$ )	$V_{hp}$	Volume of the annular heat pipe ( $\text{m}^3$ )
$c$	Centre point of Gaussian FTIR peak ( $\text{cm}^{-1}$ )	$V_m$	Volume of methanol working fluid in the heat pipe ( $\text{m}^3$ )
$f$	Oscillation frequency (Hz)	$v_T$	Volumetric flow rate ( $\text{m}^3/\text{s}$ )
$F_i$	Molar flow rate of component $i$ (mol/s)	$w$	FTIR peak width ( $\text{cm}^{-1}$ )
$h$	FTIR peak height	$x_o$	Oscillation amplitude (m)
$k_{fi}$	Forward reaction rate constant for reaction $i$ ( $i = 1, 2$ ) ( $\text{L.s.mol}^{-1}$ )	<i>Greek Letters</i>	
$K_i$	Equilibrium rate constant for reaction $i$ ( $i = 1, 2$ )	$\Delta t$	Time step size for finite difference method (s)
$m$	Reaction order	$\Delta \tau$	Step size of residence time for finite difference method (s)
$n$	Reaction order	$\mu$	Fluid viscosity (Pa.s)
$N$	Number of equivalent tanks-in-series	$\rho$	Fluid density ( $\text{kg.m}^{-3}$ )
$N_i$	Number of moles of component $i$ (mol)	$\tau$	Residence time (s)
$o$	Reaction order	$\omega_n$	Wavenumber ( $\text{cm}^{-1}$ )
$p$	Reaction order	<i>Dimensionless Groups</i>	
$q$	Reaction order	FR	Heat pipe fill ratio ( $= V_m/V_{hp}$ )
$R$	Universal gas constant ( $8.314 \text{ J.mol}^{-1}.\text{K}^{-1}$ )	$Re_n$	Net flow Reynolds number ( $= \rho v D/\mu$ )
$t$	Time (s)	$Re_o$	Oscillation Reynolds number ( $= 2\pi f x_o \rho D/\mu$ )
$T$	Temperature (K)		

no catalyst) approach. Gawande *et al* [4] reviewed the subject in detail, identifying the potential problems that may be introduced in obtaining the desired product. These include reduced yield, longer reaction times, increased energy demand to initiate reactions (e.g. high temperatures and pressures), side product formation and selectivity issues, miscibility and mixing problems, and excessive use of reagents. The alternative pathways that Gawande *et al* [4] identified for overcoming these issues were microwaves, ultrasonics, mechanochemical mixing (such as high-speed ball milling) and 'conventional and room temperature' heating (i.e. heat transfer to the reaction medium via an electric heater or from a liquid-filled jacket).

Understanding of reaction kinetics is also vital to design for industrial scale synthesis, particularly when using this solventless approach. From a chemistry perspective, it must be ascertained whether the standard kinetics models are still meaningful when the properties of the reaction medium are varying (due to the bulk change in composition during the reaction). Furthermore, from an engineering perspective, there is the requirement to safely mitigate the resulting energy released from exothermic reactions, whilst maintaining uniform mixing and good plug flow.

In a previous study [5], a new heat pipe oscillatory baffled reactor (HPOBR) and more conventional jacketed oscillatory baffled reactor (JOBR) were successfully used to thermally control an exothermic imination reaction conducted without the use of a solvent. The HPOBR demonstrated a 20-fold reduction in processing volume (due to solvent removal) and additional 13-fold improvement in reaction rate (because of the reduced dilution effect and higher operating temperature) compared with the conventional in-solvent method, leading potentially to 260-fold reduction in the required reactor volume, or 260-fold increase of throughput for the same reactor volume (in this case 6.9 mL). The present target application of the heat pipe and jacketed meso-reactors is exothermic processes involving at least one liquid phase.

The first aim of this investigation was to determine whether



meaningful kinetic data can be observed when there is no clearly defined reaction medium. Then, the secondary aim is to demonstrate the HPOBR and JOBR as platforms for quick and logical kinetic data gathering in continuous flow mode when no solvent is present. The purpose is to intensify process screening, by reducing development times and solvent usage, and establish solventless reaction operation as an approach that could be applied at all manufacturing stages of a new chemical product (from preliminary screening through to industrial scale/bespoke production). The HPOBR and JOBR both produce high levels of plug flow, which is crucial for minimising the transition times between different steady state operating conditions, thereby accelerating the screening process. This approach has previously been used in the meso-OBRR to improve development times of continuous screening compared to batch screening [6]. The mixing and heat transfer rates can also be controlled using the oscillation intensity. There is also an argument that the OBRR is "more ubiquitous" than the similar microreactor approach [7], making the HPOBR and JOBR easily adaptable to a wide range of single and multi-phase applications. The same imination reaction as the previous study [5] has again been used as a case study here.

## 2. Methodology

### 2.1. Imination reaction

The case study used for solventless reaction screening was the imination reaction between benzaldehyde and n-butylamine to form n-benzylidene-n-butylamine and water (shown in Scheme 1). This reaction exhibits a strong exothermic temperature rise, which is sufficient to exceed the boiling point of the n-butylamine (79 °C) when no solvent or thermal control is used. For reference, the estimated reaction enthalpy is  $-20 \text{ kJ/mol}$  based on average bond enthalpies [8]. The isolated imine product from this reaction consists of a pale yellow oil [9]. The

**Scheme 1.** Imination reaction between benzaldehyde and n-butylamine.

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