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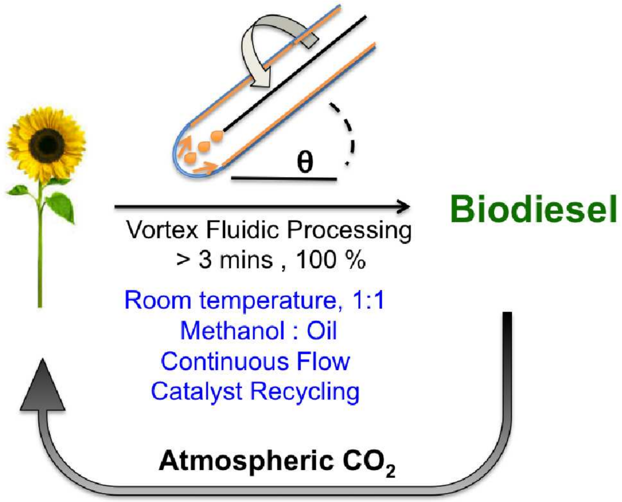

Vortex fluidic synthesis of biodiesel from sunflower oil under continuous flow at room temperature, with spontaneous phase separation.

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Continuous flow vortex fluidic production of biodiesel

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A thin film vortex fluid device (VFD) is effective in the room temperature continuous flow conversion of sunflower oil to biodiesel. Optimised VFD operating parameters affords high purity biodiesel, with no saponification, without the need for the otherwise conventional use of a co-solvent or the use of complex catalysts, with improved green chemistry metrics for biodiesel production. The biodiesel, glycerol biproduct and catalyst also spontaneously separate post-VFD processing, and the catalyst can then be readily recycled three times without the need for further complex down-streaming processing.

The combustion of fossil fuels accounts for 85 % of the global energy usage,[1,2] and with the world population exceeding seven billion in the expanding energy demanding Anthropocene era, fuel sources need to become both renewable and sustainable to avoid consequential climate change.[3] Indeed, with dwindling non-renewable fuel reserves, there has been a shift towards developing renewable energy sources including solar, tidal, wind, geothermal and biofuels. The latter is important for the transport sector, which is currently the largest consumer of crude oil.[4] Biodiesel has been put forward as an alternative fuel, being carbon neutral, non-toxic, having a high biodegradability factor and has the potential for a community or nation to become self sufficient in transport and allied energy requirments.[5-8] Biodiesel can be used in most fuel engines with little or no modifications,[9] and several countries are utilising biodiesel for their transport networks. In developing technology to satisfy the overall global need for biodiesel, green chemistry and sustainability metrics need to be adopted to ensure the impact of the processing of the fuel is minimal, and this is beginning to emerge.[10]

The production of biodiesel in 2012 was 25776 million litres and the global industry value is predicted to be $182.0 billion US by 2021.[11,12] Biodiesel is traditionally generated from vegetable oil triglycerides *via* acid or based catalysed transesterification,[13] although the rate of the base catalysed reaction is 4000 times faster than for the acid catalysed reaction.[14] Feedstocks for biodiesel production come from four areas of the plant and animal kingdoms. The first is from edible food crops such as barley and soybeans, the second is non-edible oils such as *Jatropha Curcas L,* salmon and almond oil. In India biodiesel can only be prepared from non-edible crops because of ethical issues, and in consequence a major focus there has been on the acclaimed *Jatropha* species.[6,15] The third and most promising feedstock encompasses algae, seaweed and bacteria, and the forth is animal fats.[6] The use of abundant lignocellulose is another alternative to the use of fossil carbon in generating biofuels in general, but it requires extensive catalytic processing.[16]

Current biodiesel production focuses mainly on batch processing[17,18] which requires heating,[18] the use of large excess of basic methanol, and operating under anhydrous conditions, as well as complex downstream processing to remove the catalyst, glycerol and unwanted products.[6] The use of such forcing reaction conditions in batch processing relates to the associated low mass transfer and the presence of two phases in the processing.[18,21] Related to this is the use of co-solvents such as acetone, tetrahydrafuran, dimethyl and diethyl ether, to increase the mass transfer in biodiesel production, but they can have detrimental environmental impacts.[19,20] For reasonable yields of biodiesel, the emulsion must be regulated at high temperatures and mixed using energy demanding systems such as low frequency ultrasound.[18] Not only do all of the above add expense and chemical complexity to the production of biodiesel, but the associated energy penalty limits the green chemistry metrics of the transesterification process.

Overcoming the low mass transfer as well as providing continuous flow processing of biodiesel has been established for a dynamic thin film rotating tube processor (RTP).[22,23] However, this approach requires heating, the use of dry solvents and high ratios of methanol to oil feedstock, as well as the use of condensing units to circumvent the evaporation of methanol from the system, all incurring energy penalties. In addition, spectroscopic details are limited to gas chromatography, the dimensions of the RTP are lacking, as well as any details of downstream processing.[22] Parnas *et al*. have developed a laminar flow biodiesel reactor,[21,24] which operates at high temperatures using relatively large quantities of solvent, under diffusion control. Here, high quality biodiesel is generated, albeit requiring heat input and the use of a large excess of methanol.

We have developed a continuous flow process for generating biodiesel using a vortex fluidic device (VFD), Figure 1, which is a new processing platform that display dramatic improvement in the green chemistry metrics of the transesterification process.[25] It is related to the use of the aforementioned horizontally aligned RTP, but the VFD has several additional features which facilitates the generation of biodiesel. This includes high shear rates associated with variation in the tilt angle, θ, of the 20 mm external diameter rotating tube, reduction in the relative amount of solvent required, finer control of the residence time of the liquid in the tube and significantly reduced capital outlay, at least relative to an RTP with a 6 cm diameter tube 30 cm long, which has been effective in controlling the bottom up growth of nanomaterials.[25] The VFD can operate under turbulent flow conditions, being effective in controlling chemical reactivity and selectivity for a number of organic reactions beyond diffusion control.[26-29]

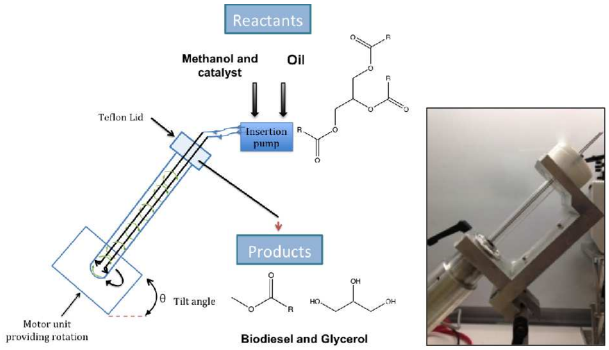

Fig 1 Schematic of the vortex fluidic device (VFD) and the transesterification process involving the catalytic conversion of oil to biodiesel (Fatty Acid Methyl Ester (FAME)), and a photograph of a VFD.

Unlike previous continuous flow methods, the VFD can operate under so call confined mode where a tube containing a finite volume of liquid is spun at high speeds (3500 rpm – 10,000 rpm), or operate under continuous flow where jet feeds deliver liquid to the base of the tube under the same conditions, Figure 1.[25] Under rapid rotation the liquid forms a dynamic thin film down to ca 200 μm thick, with the thickness depending on the rotational speed, tilt angle θ and flow rates, or volume of the liquid when operating under confined mode[27] where Stewartson/Ekman layers arise from the liquid being driven up the rotating tube with gravity forcing the liquid back.[30] Beyond organic synthesis, the utility of the VFD has been established in materials and chemical sciences, in being effective in exfoliating graphite into graphene and similarly *h*-BN,[31] coating of algal cells with graphene and magnetic polymer,[32] controlling the pore size of mesoporous silica,[32] and decorating carbon nano-onions, carbon nanotubes, and graphene with palladium nano-particles.[32]

The continuous flow mode of operation of the VFD imparts additional shear relative to the confined mode ($\theta > 0^o$) which arises from the viscous drag as the liquid whirls along the tube prior to exiting at the top. We establish that glycerol has enough translational energy to overcome the viscous drag and exit the system, thus enhancing the position of equilibrium in favour of the desired products without added complexity and energy penalty. Although the flow rates demonstrated here are lower than previous examples,[21,22] the size and the diameter of the tube can be increased as well as the possibility of using a number of the relatively inexpensive VFD platforms in parallel. Also noteworthy is the 'just in time' processing capability of the device which improves the safety of the processing. While the results potentially lay the foundation for large scale industry processing of biodiesel, the technology has more immediate use in remote locations. This relates to the nature of the feedstocks available, and the simplicity and safety of the process itself, with limited infrastructure requirements for generating renewable fuel.

Experimental

Synthesis: The VFD was equipped with a 20 mm external diameter glass tube (borosilicate glass, as a standard NMR tube). The tube was rotated at 5250 rpm at a tilt angle θ of 45 ° relative to the horizontal position, as the optimized operating parameters for shear,[25,29] with the 45 ° tilt corresponding to the maximum for the cross vector of the centrifugal force with gravity. The reactants were injected *via* automated pumps at a flow rate of 0.50 mL/min. A 10 mL solution of 1 M base (KOH, NaOH, or NaOMe in methanol) was injected through one jet feed whilst 10 ml of untreated sunflower oil was injected in *via* another parallel aligned jet feed, at the same flow rate. Products were collected in a separating funnel *via* an exit tube which resulted in instantaneous separation into three layers. The lower layer (glycerol) was removed first, followed by the middle layer (biodiesel) then the top layer (catalyst, methanol, impurities and ~10 % of the generated FAME). The oil layer was washed with 50 °C water (3 x 25 mL), 2 M $NaHCO_3$ (1 x 25 mL) and 2 M HCl (1 x 25 mL), to remove any possible free fatty acids (FFA), impurities and remaining catalyst. Conversions were calculated based on the maximum amount of biodiesel possible using 10 mL of sunflower oil. Anhydrous methanol (10 mL), dry sodium methoxide (540 mg) and dry sunflower oil (10 mL) were used under an argon atmosphere to avoid the formation of any FFA. Pure biodiesel (8.51 g) was obtained, and all experiments thereafter were directly compared, with the conversion adjusted based on the amount of starting material present in the final product, using ^{1}H NMR spectroscopy. All biodiesel was subjected to a typical "shake" test with water and a pH test to make sure that the catalyst and any possible FFA had been removed

Spectroscopy: ^{1}H and ^{13}C NMR were obtained on a 600 MHz Bruker spectrometer. Typical quantitative conditions were used (Delayed pulse (D_1) – 10.00 and Number of Scans – 64) to ascertain the purity of the biodiesel. The biodiesel gave identical spectra to that of previous published material.[35] FT-IR were recorded using a Perkin Elmer FTIR monitor. GC-MS were recorded on a Varian CP-3800 gas chromatography unit coupled with a 2200 Saturn MS detection unit. Injection occurred at 40 °C and increased at a rate of 20 °C /min until 300 °C was achieved. A reverse phase column (30 M X 25 μM X 0.25 mM) was used, and mass spectrometry data was analysed with NIST 05 molecular recognition software.

Results and Discussion

The effect of a co-solvent on the conversion to biodiesel was first investigated, as this system has high mass transfer and intense micromixing. Acetone, is such a co-solvent that has been explored in the batch processing of biodiesel to increase mass transfer,[19,20] but we found that in using the VFD, even a small amount of acetone hindered the reaction. Indeed when injecting the oil and acetone in one jet feed, with the methanol and catalyst in another, the presence of 10 % acetone completely shut down the reaction, Figure 2. Thus avoiding the use of a co-solvent and using two separate feed jets was established, improving both the environmental and financial aspects of the process, and this featured was incorporated in further optimization of the processing.

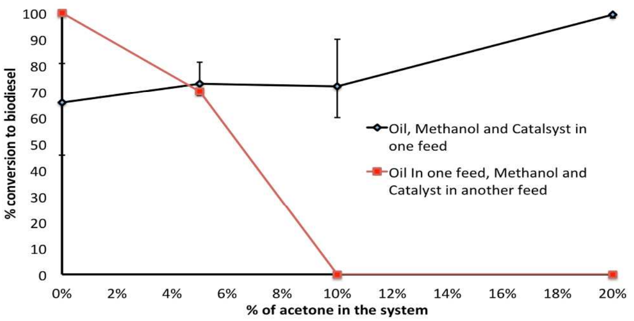

Fig 2 The effect of a co-solvent, acetone, on the conversion of pure oil into biodiesel; for the single feed experiments, 0.50 g of triolein (99.5 % purity) was used with 20 mL of 10 % KOH (in methanol) with different ratios of acetone. When two separate feeds were used, 2 mL of triolein was mixed with different ratios of acetone and injected *via* one jet feed whilst an equi-volume of 10 % KOH (in methanol) was injected *via* another parallel aligned syringe. A rotational speed of 5250 rpm was used, at θ 45^{o} relative to the horizontal position. Three separate experiments were carried out per data point.

Variation in the concentration of KOH in methanol was also studied in optimising the VFD processing. A sigmoidal relationship was observed with 0.4 M KOH giving a noticeable increase in conversion, Figure 3. A dramatic increase in conversion was observed prior to using 0.75 M KOH, and then high purity oil was generated using 1.0 M KOH. Due to the energy intensive down streaming processing required for removing glycerol, and mono- and di-glycerides, subsequent experiments focused exclusively on using 1.0 M KOH.

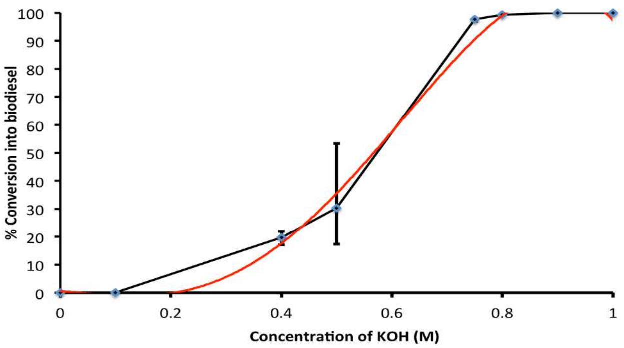

Fig 3 Variation in concentration of KOH biodiesel production from sunflower oil; 10 mL samples were used in a 1:1 ratio (oil: methanol), for a rotational speed of 5250 rpm, and θ 45^{o} relative to the horizontal position. Three separate experiments were carried out per data point.

The flow rate of reagents into the base of the VFD was varied and the product conversion monitored, Figure 4, establishing an almost linear decline in biodiesel conversion for increasing flow rate. As mentioned above, the processed liquid instantaneously separates into three layers, Figure 5. The lower level is glycerol with the highest density, ~ 1.26 g/mL, and can be readily removed, for use in a wide range of commercial applications.[36,37] The middle layer is the biodiesel, while the upper layer was shown to contain methanol, approximately 10 % of the generated FAME and the catalyst, and to further increase the green chemistry metrics of the system, recycling of the catalyst was explored. For this, the upper layer was evaporated to dryness and the residue taken up in 10 mL of methanol for the recycling process, Figure 5. This was to ensure that the volume of methanol used in each cycle was constant, thus allowing direct comparison throughout the study.

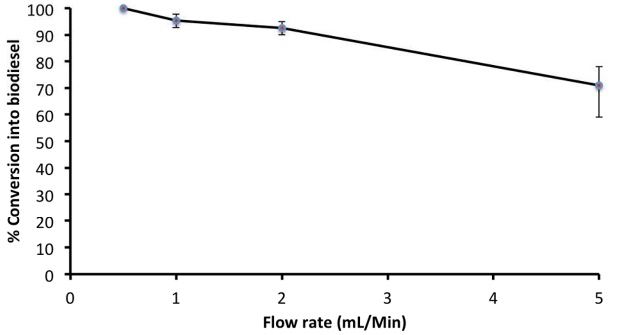

Fig 4 Effect of change in flow rate for the generation of biodiesel from sunflower oil, for a rotational speed of 5250 rpm, θ 45^{o} relative to the horizontal position, and 1.0 M KOH. Three separate experiments were carried out per data point.

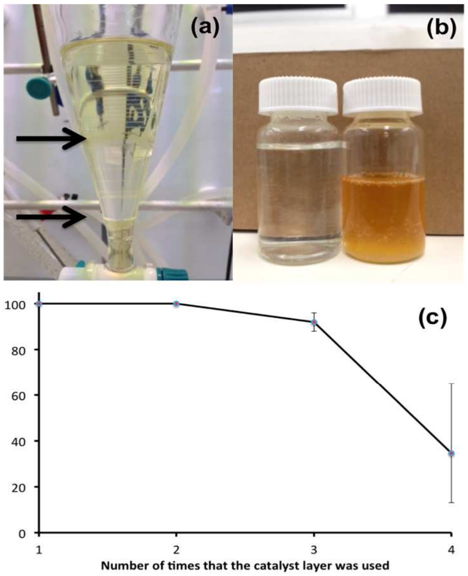

Fig 5 Photographs of (a) the three-phases separated and (b) the colour change from using pure 1 M KOH (*left)* and the catalyst recycled three times (*right)*. (c) Effect on conversion of sunflower oil to biodiesel versus the number of times of recycling the catalyst. Three separate experiments were carried out per data point.

The catalyst was introduced back into the system for further biodiesel generation without any purification after the above separation of the solvent. The percent conversion remained high at 95 % until the fourth cycle, whereupon there was a dramatic reduction in conversion to ca 22 %, Figure 5. This presumably arises from a build up in contaminants, which is evident with a change in colour, which is unaffected when neutralised with 2 M HCl. Also, the decrease in yield of the biodiesel product arises from a decrease in concentration of catalyst in the methanol layer. This is due to catalyst loss in the oil and glycerol fractions,[38] noting an increase in pH of the glycerol layer, from the expected pH of 6.9-7.6 (pKa of glycerol is ~14.2) to pH 12.28, although the effect of this is only significant after recycling four times.

Sodium hydroxide is less expensive than potassium hydroxide, and is another common catalyst used in the production of biodiesel. Indeed, replacing the KOH with NaOH in the methanol was equally effective in biodiesel production using the VFD, and heightens the cost-effectiveness of the process, with the less hygroscopic and increased safety of NaOH, further improving the green chemistry metrics of the process. Unlike previous studies, there is no need to use anhydrous solvents to eliminate water from the system, avoiding the need for a drying process on the reactants. To further highlight this, the same experiment was undertaken with water as the solvent rather than methanol. There was no hydrolysis or modification of the sunflower oil at 1.0 M or 3.0 M KOH/NaOH in water, thus establishing that we have a rather unique system. Conversion is only observed when methoxide is present. In traditional processing, water is removed from the reaction process, in minimizing the potential for water hydrolyzing alkoxide ions, and saponification. The resulting hydroxide ions can hydrolyse the sunflower oil resulting in a fatty acid salt (saponification). Even though our system is not anhydrous, it gives high purity product with no evidence for any saponification. This was further corroborated when a 50 mL sample was synthesised using anhydrous methanol and anhydrous sodium methoxide, with the yields being the same as using laboratory grade methanol and pelleted NaOH/KOH. These results suggest novel reaction pathways whereby alkoxide ions rather than hydroxide ions control the reaction, adding a new exciting dimension to synthesis of biodiesel.

Analysis of the biodiesel produced using GC-MS showed that no sunflower oil is present when using 1 M KOH. Furthermore, after the catalyst was recycled twice, mono-glycerides (MG) were present, hence a drop in yield of the biodiesel to 95 %. We have also established that the nature of the oil feedstock (saturated or non-saturated) does not affect conversion to the corresponding biodiesel methyl ester. GC-MS data show that over twenty different forms of methyl ester can be detected (ESI), suggesting that the process herein is likely to work for a range of oils and fats to produce biodiesel.

Conclusions

We have developed the use of a continuous flow vortex fluidic device for generating high purity biodiesel from sunflower oil at room temperature. This requires a simple set of conditions using cheap, caustic bases in methanol. Importantly, the process does not result in breakdown of the triglyceride fats when hydroxide is present (saponification), only alkoxides, indicating a novel pathway(s) in generating the biodiesel. Overall the process is highly efficient, with the ability to recycle the catalysts, at least three times, further increasing the green chemistry metrics of this process. Another highlight of the work is that the glycerol layer can be easily removed, based on density differentials, which also avoids the need for additional down streaming processing, in generating a usable by product.

Comparison of VFD processing with related continuous flow processing, Table 1, highlights some advantages in using the VFD. These include the much lower operating temperature and ratio of methanol to oil, without compromising on the yield, which relates to the nature of the shear within the VFD during the processing. In addition, given the low capital outlay of the VFD relative to other conventional processing, coupled with the improved green chemistry metrics of the processing, we foreshadow that the VFD has significant potential in biodiesel production.

Reactor Type	Residence time	Temperature	MeOH: Oil	Yield
Static Mixer [40]	30 mins	60 ˚C	6:1	99.8 %
Micro channel [41]	> Several mins	60 ˚C	6:1	99.0 %
Oscillatory [42]	30 mins	50-60 ˚C	1.5:1	99.0 %
Cavitational [43]	>Several seconds	60 ˚C	6:1	99.0 %
Spinning tube [44]	< 1 min	40-60 ˚C	6:1	98.0 %
Zig-Zag [45]	< 1 min	56 ˚C	9:1	99.5 %
VFD	**> Several mins**	**rt**	**1:1**	**>99.9 %**

Table 1 Comparison of VFD processing of biodiesel with related continuous flow processes.

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Notes and references

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Electronic Supplementary Information (ESI) available: ^{1}H, ^{13}C NMR, IR, and GC-MS are available for both the original sunflower oil and resulting biodiesel. See DOI: 10.1039/c000000x/

1. L. Starke, Worldwatch Institute, State Of The World, W.W Norton and Co., 2009.
2. International Energy Agency, Key world energy statistics, Paris, 2007.
3. World Population Prospects: The 2010 revision, United Nations, 2010.
4. C. H. Christensen, J. Rass-Hansen, C. C. Marsden, E. Taarning and K. Egeblad, *ChemSusChem,* 2008, **1**, 283-289.
5. J. Song, M. Alam and A. L. Boehman, *A. Combust. Sci. Technol.,* 2007, **179**, 1991-2037.
6. A. P. Vyas, J. L. Verma and N. Subrahmanyam, *Fuel*, 2010, **89**, 1-9.
7. A. A. Kiss, A. C. Dimian and G. Rothenburg, *Adv. Synth. Catal.*, 2006, **348**, 75-81.
8. T. Holloway and M. Johnston, *Environmental Science and Technology*, 2007, **41**, 7967- 7973.
9. J. P. Szybist, J. Song, M. Alam and A. Boehman, *Fuel Processing Technology,* 2007, **88**, 679-691.
10. S. Luduc, K. Natarajan, E. Dotzauer, I. McCallum and M. Obersteiner, *Appl. Energ.,* 2009, **86**, s125-s131.
11. A. Avinash, D. Subramaniam and A. Murugesan, *Renew. Sust. Energ. Rev.* 2014, **29**, 517- 527.
12. Navigant Research, http://www.navigantresearch.com/ (accessed 23rd April 2014).
13. A. Demirbas, *Prog. Energy Combust. Soc.,* 2005, **31**, 466-487.
14. M. W. Formo, *J. Am. Oil. Chem. Soc.*, 1954, **31**, 548-549.
15. S. P. Singh and D. Singh, *Renew. Sust. Energ. Rev.,* 2010, **14**, 200-216.
16. J. Q. Bond et al., *Energy Environ. Sci*., 2014, **7**, 1500-1523.
17. J. M. Marchetti, V. U. Miguel and A. F. Errazu, *Renew. Sust. Energ. Rev.,* 2007, **11**, 1300-1311.
18. J. V. Gerpen, *J. Fuel. Process. Technol.,* 2005, **86**, 1097-1107.
19. G. Guan, N. Sakurai and K. Kusakabe, *Chemical Engineering Journal,* 2009, **146**, 302-306.
20. L. T. Thanh, K .Okitsu, Y. Sadanaga, N. Takenaka, Y. Maeda and H. Bandow, *Fuel*, 2013, **103**, 742-748.
21. M. B. Boucher, C. Weed, N. E. Leadbeater, B. A. Wilhite, J. D. Stuart and R. S. Parnas, *Energy and Fuels,* 2009, **23**, 2750-2756.
22. H. Lodha, R. Jachuck and S. S. Singaram, *Energy and Fuels,* 2012, **26**, 7037-7040.
23. X .Chen, N. M. Smith, K. S. Lyer and C. L. Raston, *Chem. Soc. Rev.*, 2014, **43**, 1387-1399.
24. S. A. Unker, M. B. Boucher, K. R. Hawley, A. A. Midgette, J. D. Stuart and R. S. Parnass, *Bioresource Technology,* 2010, **101**, 7389-7396.
25. L. Yasmin, X. Chen, K. A. Stubbs and C. L. Raston, *Scientific Reports*, 2013, **3**, 2282.
26. L. Yasmin, T. Coyle, K. A. Stubbs and C. L. Raston*, Chem Commun*., 2013, **49**, 10932 –10934.
27. M. N. Gandy, C. L. Raston and K. A. Stubbs, *Org. Biomol. Chem.,* 2014. DOI: 10.1039/c40ob00926.
28. L. Yasmin, P. K. Eggers, B. W. Skelton, K. A. Stubbs and C. L. Raston, *Green Chem*., 2014, **16,** DOI: 10.1039/c4gc00881b.
29. L. Yasmin, K. A. Stubbs and C. L. Raston, *Tetrahedron Letters*, 2014, **55**, 2246–2248.
30. D. A. Bennetts and L. M. Hocking, *Proc. R. Soc. London*, 1973, **333**, 469-489.
31. M. H. Wahid, E. Eroglu, X. Chen, S. M. Smith and C. L. Raston, *Green Chem.*, 2013, **15,** 650-655.
32. M. H. Wahid, E. Eroglu, X. Chen, S. M. Smith and C. L. Raston*., RSC Adv.*, 2013, **3,** 8180 – 8183.
33. C. L. Tong, R. A. Boulos, C. Yu, K. S. Iyer, and C. L. Raston, *RSC Adv*., 2013, **3**, 18767 -18770.
34. X. Chen, W. Zang, K. Vimalanathan, K. S. Lyer and C. L. Raston, ,*Chem. Commun*., 2013, **49,** 1160-1162.
35. S. Basumatary, P. Barua and D. C. Deka, *J. Chem. Pharm. Res*., 2013, **5**, 172-179.
36. M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi and C. D. Pina, *Angew. Chem. Int. Edit.,* 2007, **46**, 4434 –4440.
37. J. A. Kenar, *Lipid Technology*, 2007, **19**, 249-253.
38. A. K. Singh and S. D. Fernando, *Chem. Eng. Technol.,* 2007, **30,** 1716-1720.
39. Z.Qiu, L. Zhao and L. Weatherley, *Chem. Eng. Process.,* 2010, **49,** 323-330.
40. J.C. Thompson and B.B. He, *T. ASABE.,* 2007, **50,** 161-165.
41. J. Sun, J. Ju, L. Ji, L. Zhang, N. Xu, *Ind. Eng. Chem. Res*., 2008, **47,** 1398–1403.
42. A.P. Harvey, M.R. Mackley and T. Seliger, *J. Chem. Technol. Biotechnol*., 2003, **78,** 338–341.
43. US 2009/0043118 A1, 2009.
44. H. Lodhar, R. J. J. Jachuck*, Proceedings of the AIChE Annual Meeting*, Salt Lake City, USA, 2007.
45. Z. Wen, X. Yu, S.-T. Tu, J. Yan and E. Dahlquist, *Bioresour. Technol.,* 2009, **100,** 3054-3060.