In collaboration with Massachusetts Institute of Technology

Sono-Chemical Reactor Design for Biodiesel Production via Transesterification

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INTRODUCTION

- Biodiesel is an alternate fuel having high potential of substituting fossil based fuels.
- Biodiesel is produced from the transesterification reaction occurring between lipids and alcohols in the presence of a basic or acidic catalyst.

$C_{54}H_{104}O_6$ (Veg. Oil) + 3 CH_4O (Meth.) $\rightleftharpoons$ 3 $C_{18}H_{36}O_2$ (FAME) + $C_3H_8O_3$ (Glycerol)

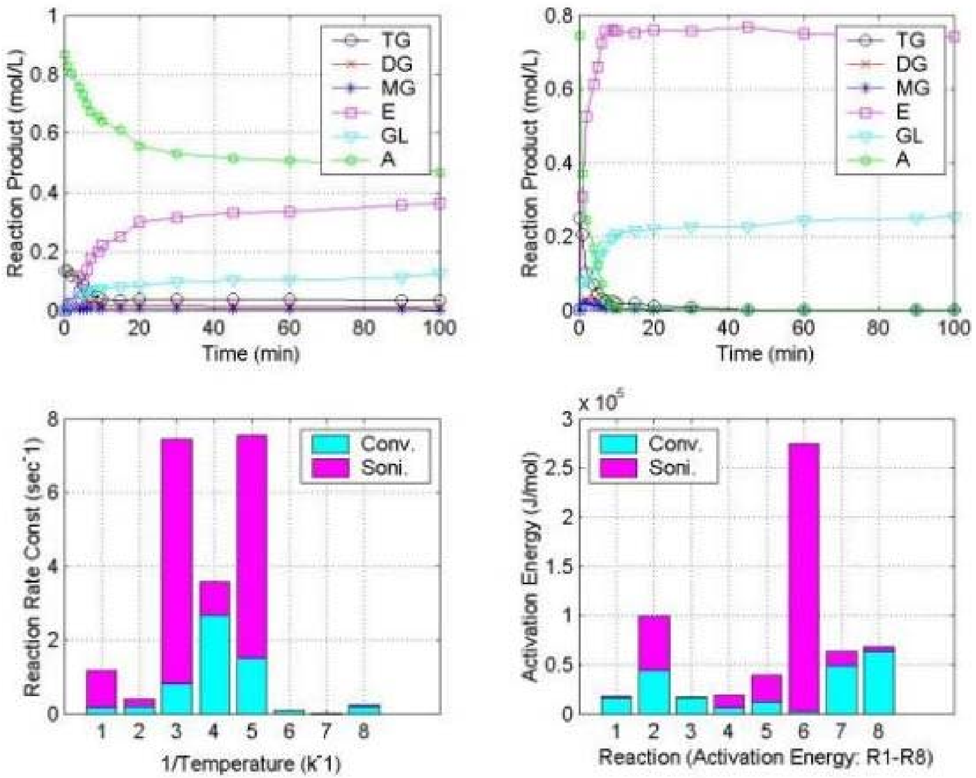
- The source of the lipid is largely vegetable oils such as palm, sunflower, soybean etc.and also waste cooking oils.
- The reaction is a slow moving and reversible which requires mechanical agitation or at the cost of higher reactant agent. This can be provided by either a stirrer or by circulation in a flow-channel-reactor.
- To overcome this problem associated with conventional methods, the use of ultrasound has been suggested and applied by many researchers successfully.

$$\text{Triglyceride} + \text{Alcohol} \underset{K2}{\overset{K1}{\rightleftharpoons}} \text{FAME} + \text{Diglyceride} \qquad (1)$$

$$\text{Diglyceride} + \text{Alcohol} \underset{K4}{\overset{K3}{\rightleftharpoons}} \text{FAME} + \text{Monoglyceride} \qquad (2)$$

$$\text{Monoglyceride} + \text{Alcohol} \underset{K6}{\overset{K5}{\rightleftharpoons}} \text{FAME} + \text{Glycerol} \qquad (3)$$

$$\text{Triglyceride} + 3\text{Alcohol} \underset{K8}{\overset{K7}{\rightleftharpoons}} 3\text{FAME} + \text{Glycerol} \qquad (4)$$



Comparison of conventional and sonication transesterification at 60°C and their evaluated reaction constants and activation energies [Janajreh et al]

MECHANISM

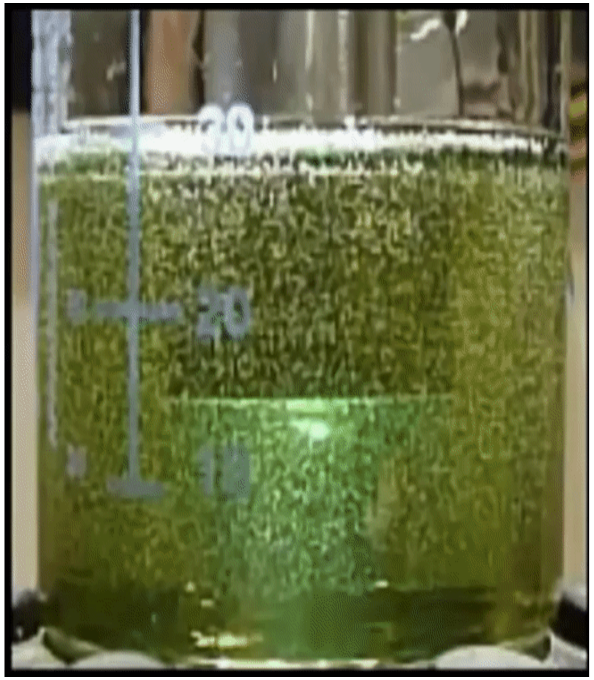
- Sonochemistry is a process intensification technique which uses ultrasound waves for accelerating chemical reactions.

- The wave causes intense cycles of compression and rarefaction at micro levels in the fluid volume creating cavitation voids or bubbles that contain highly activated vapors of the reactants.

- The temperature and pressure in these micro bubbles can reach as high as 5000 K and 1000 atm [1].

- Millions of such bubbles are formed as soon as the sonication is applied.

- When these bubbles implode they cause tremendous localized increase in mass transfer which intensify the reaction with a rate several orders higher than the conventional or stirring flow cases.



[1] V. G. Gude, G. E. Grant. “Biodiesel from waste cooking oils via direct sonication”, Applied Energy, 2013,109, 135-144.

LITERATURE REVIEW

- Stavarache et al. [2] reported higher yields in shorter time using ultrasonic transesterification under homogeneous catalysts of NaOH and KOH and for the same molar ratio and catalyst amount compared to conventional stirring method.
- Manickman et al. [3] reported that mechanical agitation takes triple the time to give 78% yield as weighed to ultrasonic transesterification which gives about 93% yield with 1% KOH and 3:1 methanol to oil molar ratio.

There are many simulation works that have carried out of sono-chemical reactors.

- Jordens et al. [4] used the complex wave number approach to design a continuous flow sonochemical reactor for degradation of CCl4 (Carbon Tetra-chloride). They tested their design at multiple frequencies, rated power and also multiple transducers. Millions of such bubbles are formed as soon as the sonication is applied.
- Jamshidi et al. [5] used the complex wave number approach to simulate acoustic phenomena in a continuous flow sonochemical reactor for homogenizing nano particle solutions. They tested different geometries for optimizing the reactor design.

[2] C. Stavarache, M. Vinatoru, Y. Maeda, "Ultrasonic versus silent methylation of vegetable oils", Ultrasonics Sonochemistry, vol. 13, pp. 401-407, 2005.

[3] S. Manickam, V. N. D Arigela, P. R. Gogate, "Intensification of synthesis of biodiesel from palm oil using multiple frequency ultrasonic flow cell", Fuel Processing Technology, vol. 128, pp. 388- 393, 2014.

[4]J. Jordens, A. Honings, J. Degrève, L. Braeken, and T. V. Gerven. "Investigation of design parameters in ultrasound reactors with confined channels", Ultrasonics Sonochemistry, 2013, 20, 1345-1352.

[5] R. Jamshidi, B. Pohl, U.A. Peuker, G. Brenner, Numerical investigation of sonochemical reactors considering the effect of inhomogeneous bubble clouds on ultrasonic wave propagation, Chem. Eng. J. 189–190 (2012) 364–375.

OBJECTIVE

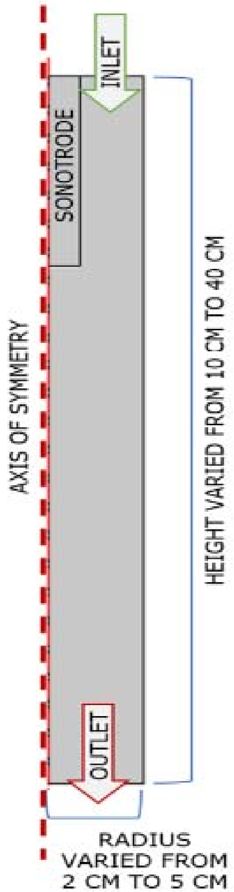
1
- To extend the common batch reactor processing to continuous reactors targeting larger production.

2
- To simulate the working of a continuous sono-chemical reactor while integrating both sonication and reaction flow.

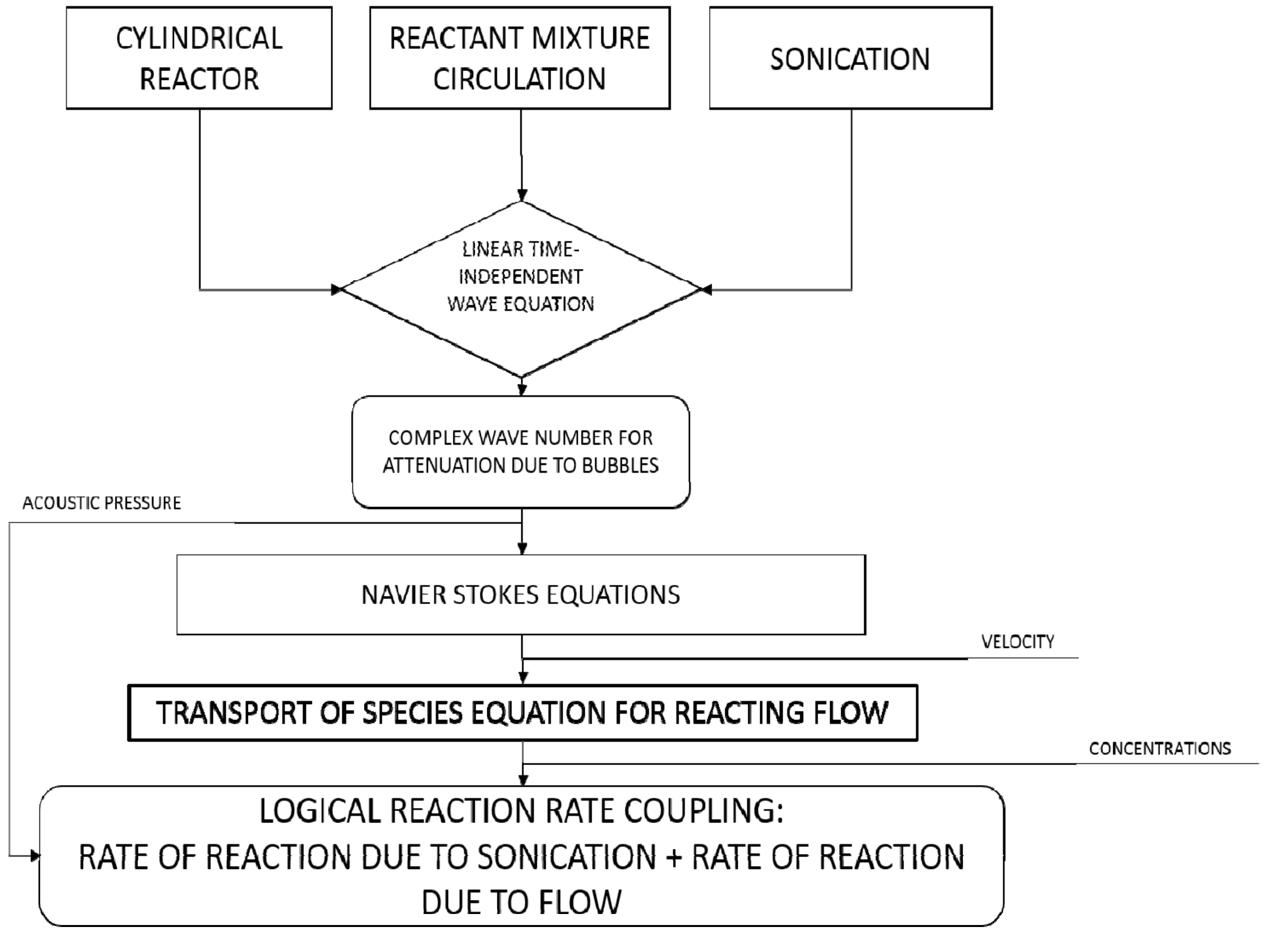
3
- Investigate the acoustic pressure and the rate constant of the sonication.

4
- Conduct sensitivity analysis: i.e. effect of geometry, rated power and frequency is carried out.

PROBLEM SETUP



METHODOLOGY



MATHEMATICAL SETUP & BC

ACOUSTIC

$$\nabla^2 P + {k_c}^2 . P = 0$$

$${k_c}^2 = \frac{\omega^2}{C^2}\left(1 + 4\frac{\pi C^2 n_b R_b}{{\omega_o}^2 - \omega^2 + 2ib\omega}\right)$$

$$C = \sqrt{\frac{K_E}{\rho_E}}$$

REACTIVE FLOW

$$\rho(\boldsymbol{u}\nabla\boldsymbol{u}) = -\nabla P_{flow} + \mu\nabla^2\boldsymbol{u} + \rho\boldsymbol{g}$$

$$\nabla(-D\nabla c_i) + \boldsymbol{u}\nabla c_i = R_{rate}$$

KINETIC

$$k_{flow} = A.e^{\frac{-E}{R_u T}}$$

$$k_{son} = A.e^{\frac{-E}{R_u . T_{bubble}}}$$

$$T_{bubble} = \frac{T_L P(\gamma - 1)}{P_{vapor}}$$

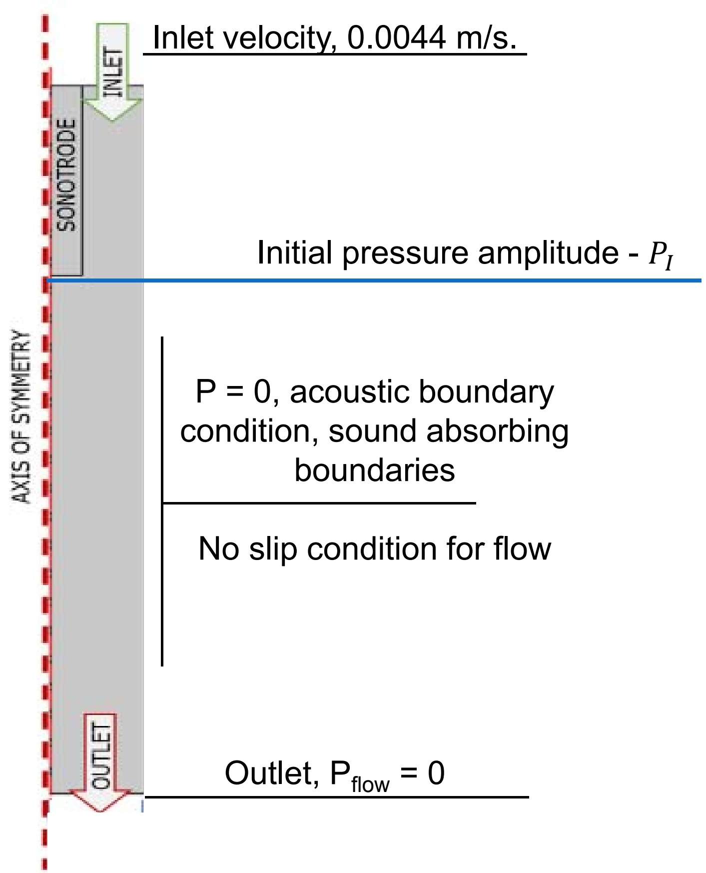
$$-R_{rate} = [(P > P_{blake})\beta\, k_{son} * [Oil]^2 + (1 - \beta)k_{flow} * [Oil]^2]$$

$$\beta \approx 2x10^{-9}P \qquad for\ p_{blake} < P < 1x10^8\ Pa.$$

LOGICAL COUPLING

P is the acoustic pressure,
P_D is the rated power
ρ_E is the effective density
C is Equivalent speed of sound in the medium
A_r area of transducer
ω is the angular frequency,
μ is the viscosity
K_E is the effective bulk modulus
k_c is the complex wave number
n_b number of bubbles
b is damping coefficient
k_{son} is the sonication rate constant
T_{bubble} is the cavitation bubble temperature
γ is the specific heat ratio
P_{vapor} is the vapor pressure.
K is the rate constant
A is the pre-exponential factor
E is the activation energy
R_u is the universal gas constant
T is the temperature.
u is the velocity field
g is the gravitational acceleration
P_{flow} is the pressure
D is the diffusion coefficient
c_i is molar concentration
R_{rate} is the rate of reaction
β is the cavitation bubble volume

BOUNDARY CONDITIONS

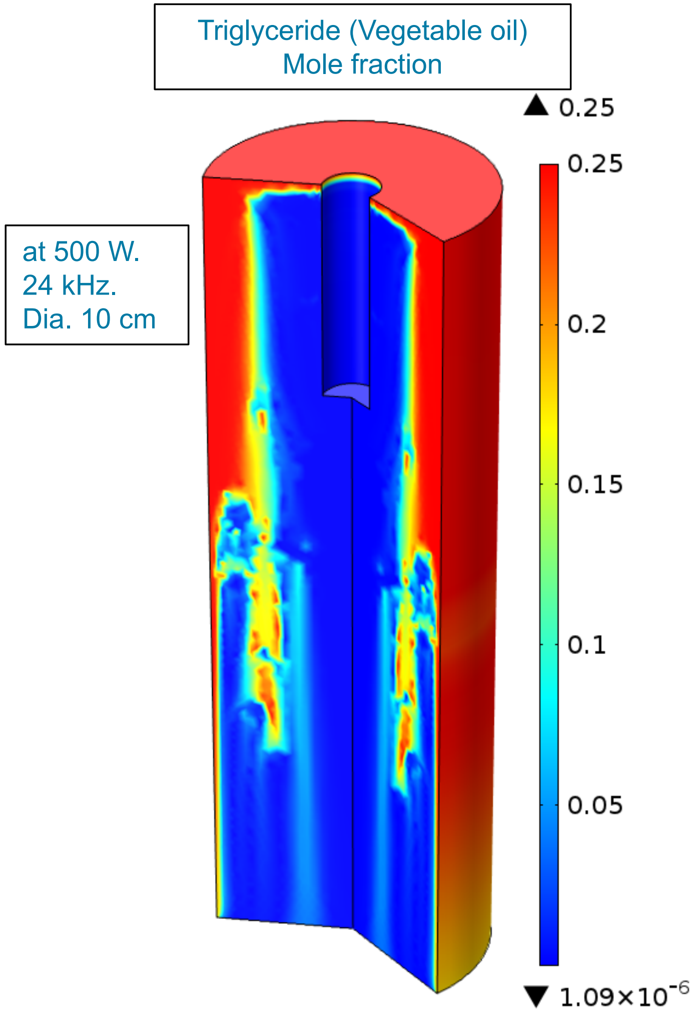


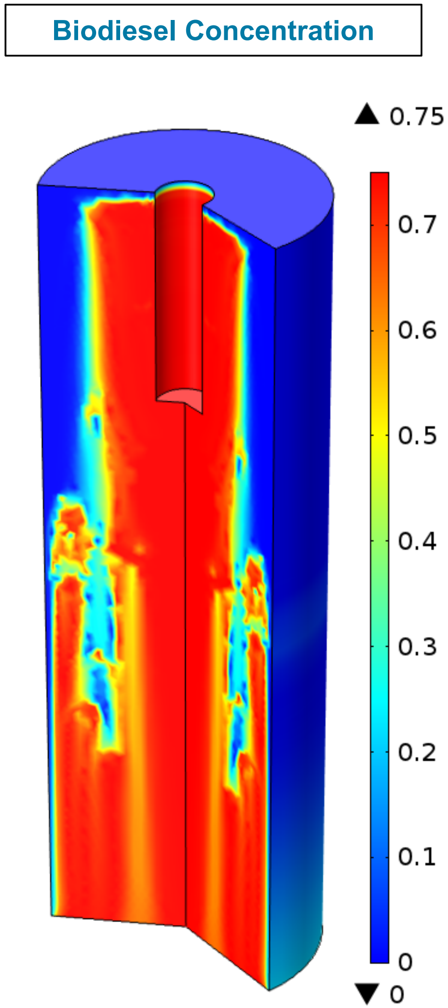
$$P_I = \sqrt{\frac{2\rho_E C P_d}{A_r}}$$

ρ_E is the effective density
C is Equivalent speed of sound in the medium
P_d is the dissipated power in Watt
A_r area of transducer

Mesh Sample

RESULTS – SPECIES DISTRIBUTION

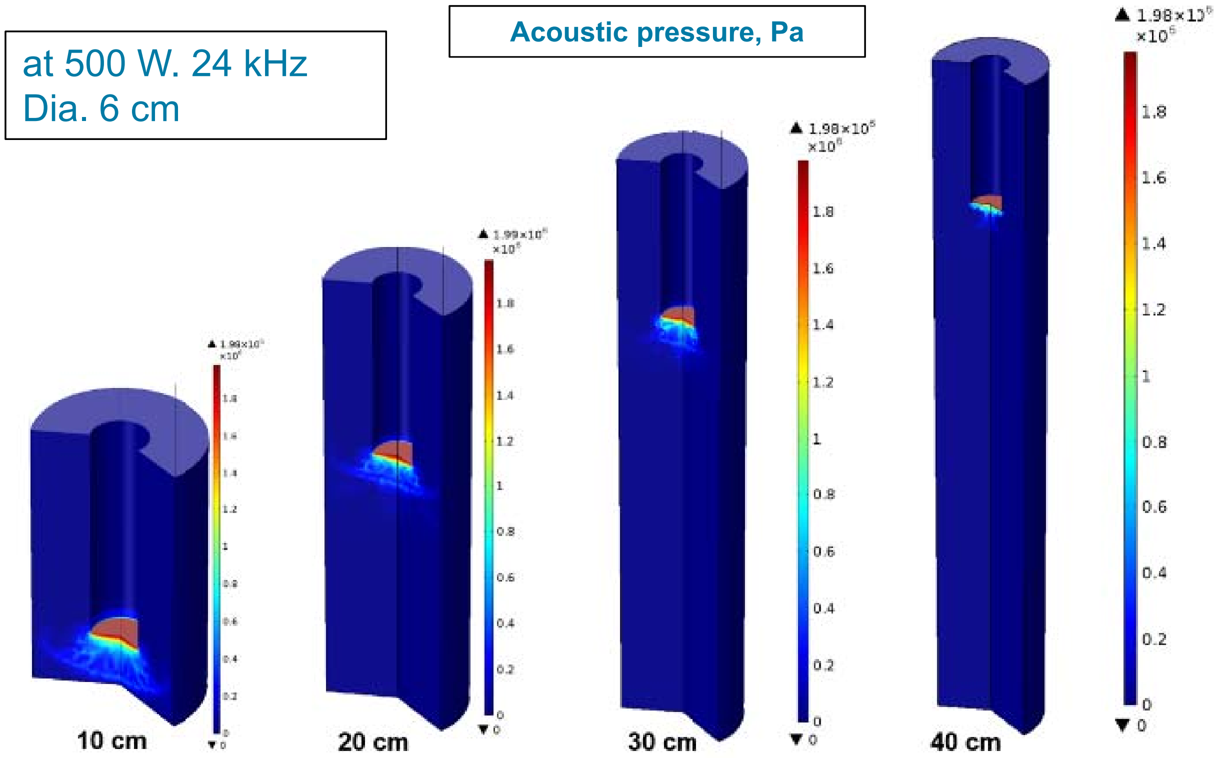




1. Biodiesel formation begins at the very tip of the sonotrode.
2. Biodiesel mole fraction is higher in the central section of the reactor due to the placement of the sonotrode.
3. Maximum of vegetable oil is converted before reaching the sonotrode tip.

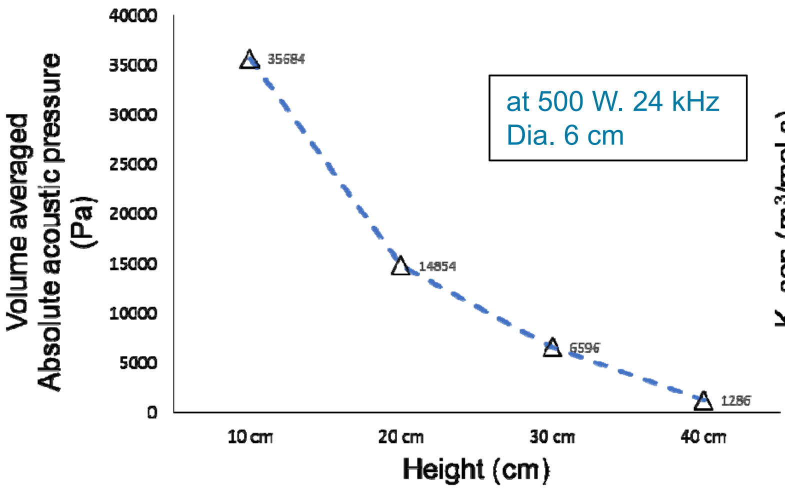
RESULTS – EFFECT OF HEIGHT

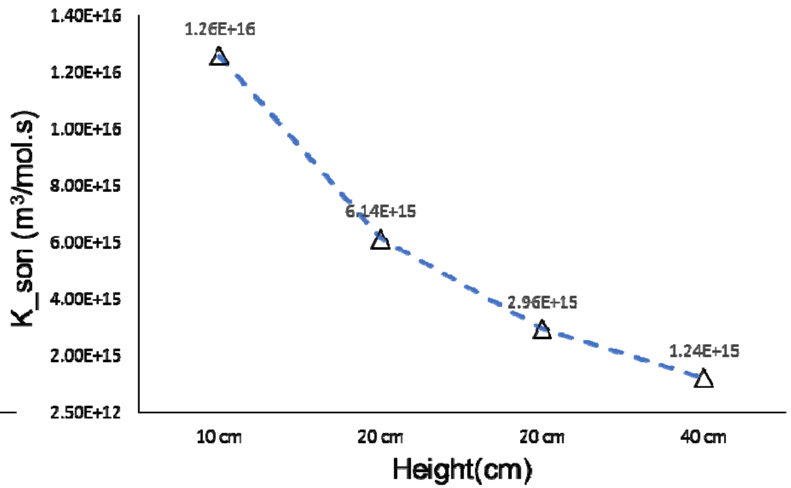
at 500 W. 24 kHz
Dia. 6 cm



1. The height was varied from 10 cm to 40 cm in steps of 10 cm.
2. Due to cavitation bubble attenuation, higher acoustic pressures were observed in regions close to the sonotrode.
3. For taller reactors, the lower regions of the reactor experienced much less acoustic activity obviously due to the attenuation from the cavitation bubbles
4. The peak acoustic pressure obtained in all the cases was more or less similar at 1.98 MPa.

RESULTS – EFFECT OF HEIGHT





Max. VA. Acoustic pressure :
36 kPa (10 cm height)

Min. VA. Acoustic pressure :
1.3 kPa (40 cm height)

Max. VA. K_son:
1.26E16 m3/mol.s (10 cm height)

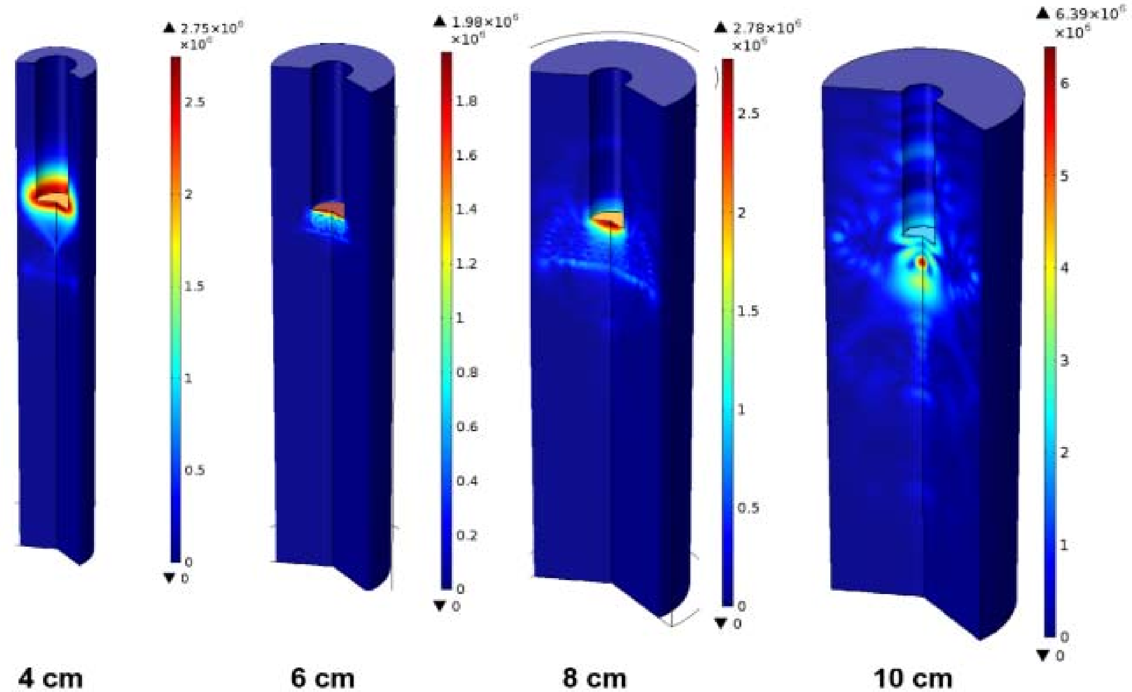
Min. VA. K_son:
1.24E15 m3/mol.s (40 cm height)

Max Cavitation bubble temp. = 2700 K

1. To normalize the changes in volume among the cases the volume averaged acoustic pressure was studied.
2. Volume averaged acoustic pressure decreased with increase in reactor height.
3. The best acoustic pressure (volume averaged) was for the reactor with 10 cm height and it was 36 kPa and the least was 1.3 kPa for the height of 40 cm.
4. K_son results also showed similar variations as the volume averaged acoustic pressure.

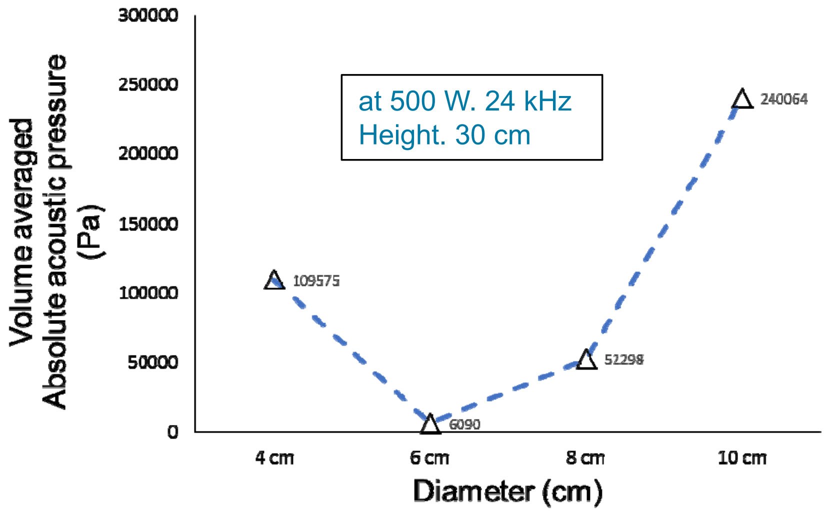
RESULTS – EFFECT OF DIAMETER

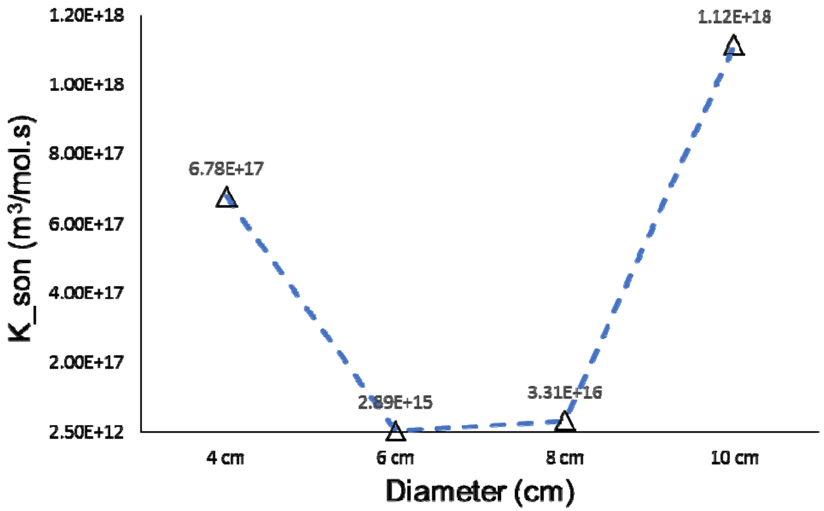
at 500 W. 24 kHz
Height. 30 cm



1. The diameter was varied from 4 cm to 10 cm in steps of 2 cm.
2. Unlike the results of height variation, the acoustic pressure did not show a decreasing trend with increase in diameter.
3. For the cases of diameters 8 cm and 10 cm the acoustic pressure distribution was more widespread, whereas for the diameters of 4 cm and 6 cm the acoustic pressure was concentrated close to the sonotrode due to their narrower design.
4. The attenuation is more prominent in the vertical axis as compared to the radial axis.
5. The acoustic pressure at the boundaries is absorbed by the walls due to the sound absorbing boundary condition.
6. With larger diameters more fluid is exposed to the acoustic energy hence the pressure distribution is widespread.

RESULTS – EFFECT OF DIAMETER





Max. VA. Acoustic pressure :
240 kPa (10 cm Dia.)

Min. VA. Acoustic pressure :
6.1 kPa (6 cm Dia.)

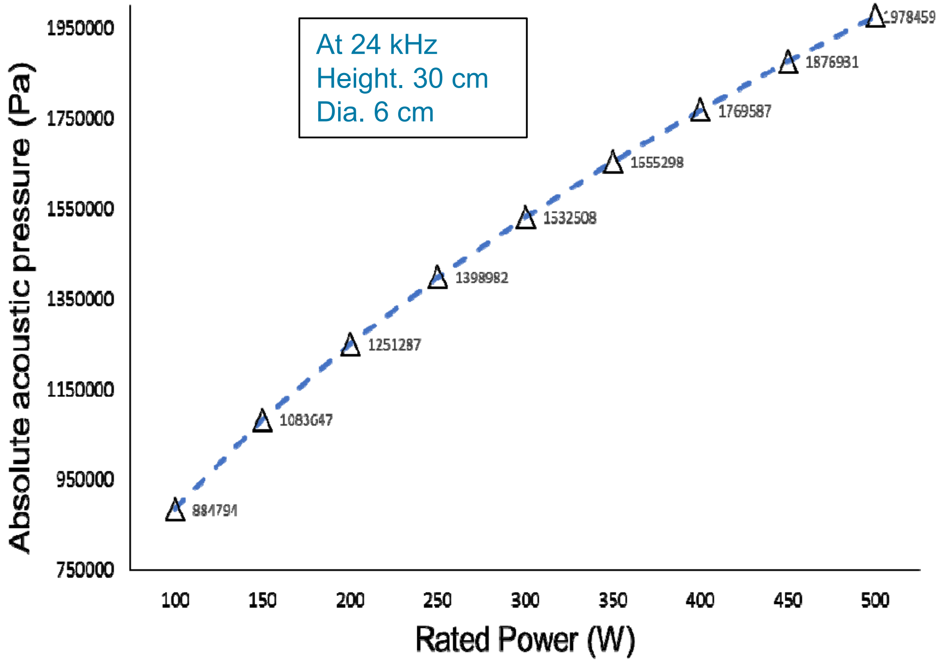
Max. VA. K_son:
1.2E18 m3/mol.s (10 cm Dia.)

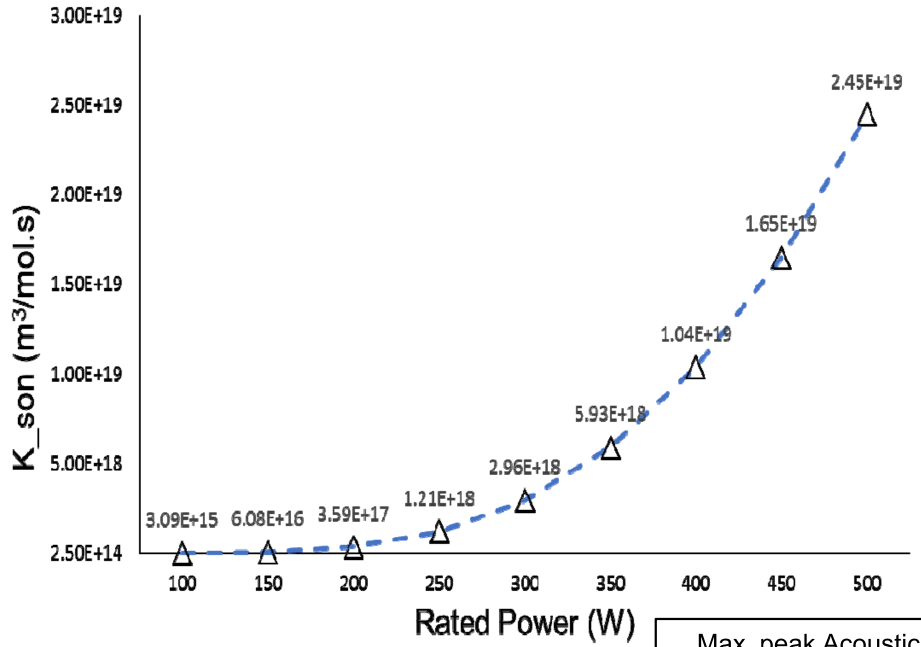
Min. VA. K_son:
2.9E15 m3/mol.s (6 cm Dia.)

Max Cavitation bubble temp. = 8827 K

1. With varying diameter the cavitation profiles tend to be more complex and lack a well-defined relation with the diameter increase.
2. This phenomena is reflected in the volume averaged acoustic pressures, since they are not following a particular order.
3. K_son variation with diameter adhered to the same profile of the volume averaged acoustic pressure.
4. The results from this analysis show that having larger diameters can be beneficial under the considered boundary conditions.
5. However much larger diameters call for higher flow rates. These results are suitable for sonication equipments which can process fluids with flow rate of 10 to 50 L/hr.

RESULTS – EFFECT OF RATED POWER





Max. peak Acoustic pressure : 1.9 MPa (500 W)

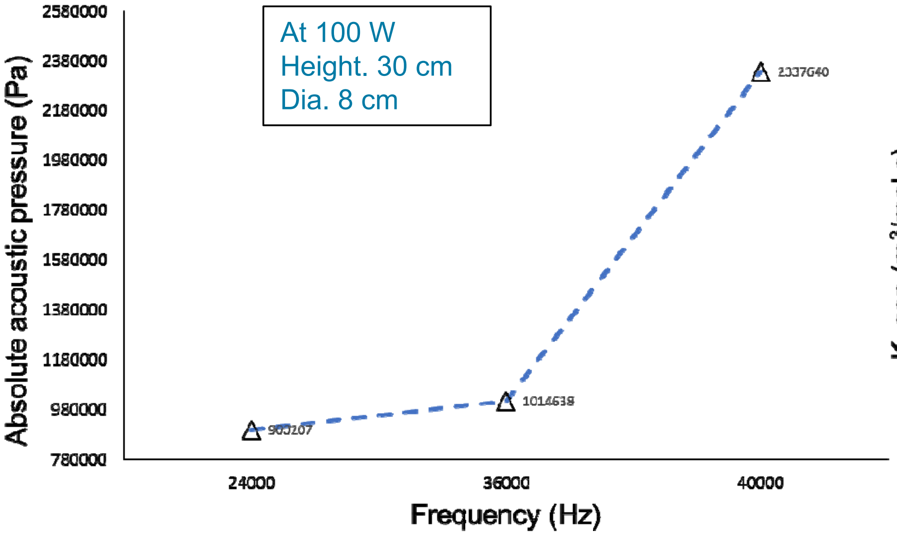
Min. peak Acoustic pressure : 0.88 MPa (100 W)

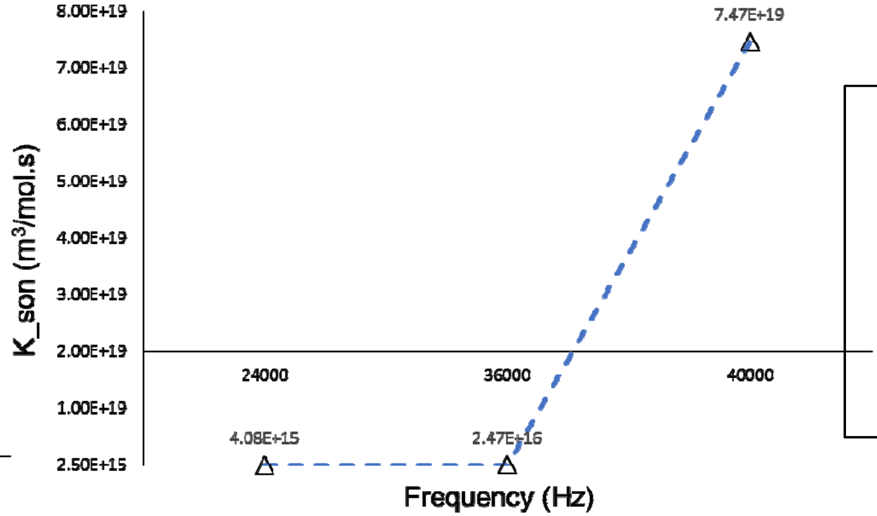
Max. K_son: 2.9E19 m3/mol.s (500 W)

Min. K_son: 3.1E15 m3/mol.s (100 W)

1. The rated power was varied from 100 to 500 W in steps of 50 W.
2. Direct relationship of acoustic pressure and K_son is seen with increase in rated power.

RESULTS – EFFECT OF FREQUENCY





Max. peak Acoustic pressure : 2.3 MPa (40 kHz)

Min. peak Acoustic pressure : 0.9 MPa (24 kHz)

Max. K_son: 7.5E19 m3/mol.s (40 kHz)

Min. K_son: 4.8E15 m3/mol.s (24 kHz)

1. Three frequencies i.e. 24,000 Hz, 36,000 Hz and 40,000 Hz are considered.

2. The results indicated increasing values of peak acoustic pressure and K_son with increase in frequency, but the proportion of increment was not stable.

3. The gain in peak acoustic pressure between 24,000 Hz and 36,000 Hz was lower than the gain between 36,000 Hz and 40,000 Hz.

4. This unpredictable variation is by the change in the complex wave number for every case of frequency, since frequency is a variable used in the calculation of wave number.

5. In addition to this the change in cavitation bubble volumes with varying frequency also affects the acoustic pressure.

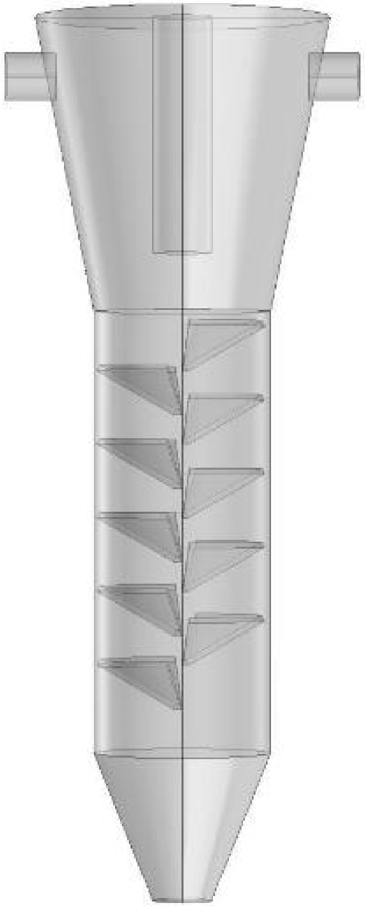
Jordens, A. Honings, J. Degrève, L. Braeken, and T. V. Gerven. “Investigation of design parameters in ultrasound reactors with confined channels”, Ultrasonics Sonochemistry, 2013, 20, 1345-1352.

CONCLUSION

- In this work a design for continuous sonochemical reactor for biodiesel production from vegetable oils was evaluated through numerical modelling.
- The ultrasound wave was simulated with the Helmholtz equation. A complex wave number was used to account for the attenuation due to cavitation bubbles. Coupled Navier-Stokes and species equation were used to model the reactive flow. The Arrhenius kinetic principle was used to evaluate the reaction kinetics of the flow and also the bubble.
- A sensitivity analysis based on height, diameter, rated power and frequency was carried out to optimize the acoustic and reactive characteristics of the reactor.
- It was observed that for taller reactors, the acoustic activity did not reach to the lower region of the reactor due to attenuation from cavitation bubbles.
- For increase in diameter the acoustic pressure distribution was wide spread implying lower attenuation in radial direction.
- Acoustic pressure increased with increase in rated power.
- For frequency increase, the acoustic pressure increased but with some unpredictability.
- The reaction rate constant for sonication showed similar results as acoustic pressure in all cases due to its dependency on acoustic pressure.
- For the current study we found an optimized design with 10 cm diameter, 30 cm height. At this geometric condition the acoustic pressure and K_son were observed to be the highest. (for flow rate of 10 – 50 L/hr)

EXPERIMENTAL SETUP

FUTURE DESIGN



THANK YOU

APPENDIX – PROPERTY TABLE

Property	Unit	Value
Activation energy, E	J/Mol	164958.4
Adiabatic coefficient, γ	-	1.4
Ambient liquid pressure, P_{liq}	Pa	1.00E+05
Blake threshold P_{blake}	Pa	1.00E+05
Oil density	Kg/m^3	883
Dynamic viscosity of oil	Pa.s	1.62E-02
Density of methanol	Kg/m^3	883
Dynamic viscosity of methanol	mPa.s	0.545
Pre-exponential factor A	$m^3/mol/s$	3.49E+22
Vapor pressure of vegetable oil	Pa	543
Vapor pressure of methanol	Pa	13020
Universal gas constant R_u	J/mol.K	8.314
Bulk modulus of Methanol	N/m^2	0.8E9
Bulk modulus of Oil	N/m^2	2.1E9
Surface tension of methanol, σ	N/m	0.002250
Thermal diffusivity of the methanol, D	m^2/s	5.9E-08