ENERGY – PART I

01 April 2013

M.Sc. Course on Process Intensification





Fundamentals of Process Intensification PRINCIPLES (GOALS) optimizing the driving maximizing the maximizing giving each molecule effectiveness of forces and maximizing synergistic effects the same processing the specific surface intra- and from partial experience areas to which these intermolecular processes forces apply events **APPROACHES SYNERGY** TIME **STRUCTURE ENERGY** (spatial (thermodynamic (functional (temporal domain) domain) domain) domain) 10⁻² 10° 10² SCALES Cata yst/reaction processes, particles, thin Ims **Processing units** Hydrodynamics and Molecular Processing transport processes, processes plant/site single- and multiphase system. **10**⁻⁴ **10**° 10-2 m **MOLECULAR MESO** MACRO

MOLECULAR SCALE

01 April 2013

M.Sc. Course on Process Intensification





Energy transfer to molecules



Energy transfer to molecules



Embryonic stage: Nobel prizes won



Laser beams to control molecules



Chlorination of methane: difficult + mostly by rebounding collisions



Laser-induced vibration: C-H bond stretching, making the target molecule "bigger" for collisions + introducing stripping collisions: reaction rate x 100

01 April 2013

M.Sc. Course on Process Intensification

6

Simpson et al. 1996; Kandel & Zare, 1998; Hoffmann, 2000



Energy transfer to molecules





Laser beams to control molecules

In HOD molecule by changing the colour of the laser beam either O-H or O-D bond can be broken





Three modes of vibration of a water molecule:

Bend

Symmetric stretch

Asymmetric stretch

01 April 2013

M.Sc. Course on Process Intensification



8

Vanderwal & Crim, 1990; Metz et al. 1993; Hoffman, 2000

MESO SCALE

01 April 2013

M.Sc. Course on Process Intensification

9



Energy to enhance mesoscale effects





Contents

- Energy of electric field
- Energy of magnetic field
- Energy of electromagnetic field (microwaves, light)
- Energy of acoustic field (ultra-/infrasound)
- Energy of flow field (cavitation, supersonic shockwave)
- Energy of high gravity (next lecture)





(Pulsed) electric fields in chemical processing

Bringing electric charge to the droplets and particles

Mechanisms and effects:

- increased rate of droplet detachment, so that drop sizes are reduced and interfacial area per unit volume is increased.
- acceleration of the drop velocity through the continuous phase under the influence of an EHD force.
- reduction in the effective interfacial tension and the existence of an electrical potential gradient at the interface, promoting circulation and interfacial turbulence
- enhanced coalescence under the influence of the EHD forces.
 - extraction rate enhancements of 200-300% reported in liquid-liquid extraction
 - in electric-field-induced emulsification 200 to 500 times increase in the surface area per unit volume, compared to the millimeter-sized droplets in the conventional processes (T. C. Scott, Sep Purif Methods, 18, 65-109 (1989)

01 April 2013

M.Sc. Course on Process Intensification



12





Application of electric field





(a) At 0.0 ms

(f)At 4.45 ms







(a) t = 0 ms

(l) t

- Drop deformation (dispersion)
 - Using electric field strength > 4.5 kV/cm → droplets size decreases (~5 µm)
 - Smaller droplets accelerated and have mixing pattern → increase mass transfer (30-40%)
- Electro-extractor:
 - on lab scale, the extraction efficiency is higher than in conventional extractor column.
 - No large scale electro-extractor is known

- Drop coalescence
 - Using electric field strength < 1.8 kV/cm→ drop size increases
- Electro-coalescer:
 - On lab scale, separation efficiency increases (from 5% to 85%)
 - On large scale, settling time reduces from 3 h to 10 min

01 April 2013

M.Sc. Course on Process Intensification



- Dispersion: Ghadiri, 2003a; Scott, 1988, 1989b
- Coalescence: Ghadiri, 2001; Bailey, 1986



Gliding Arc Technology (GlidArc)





Typical Parameter Values/Limits:

gas velocities: typically greater than 10 m/s

- New way of plasma generation by formation of electric "gliding discharges".
- At least two electrodes diverging with respect to each other are placed in fast gas flow and in the flow direction. Gliding discharges are produced between the electrodes and across the flow.



Electric Fields in Micro World

Electro-hydrodynamic mixing

(Oak Ridge National Laboratory)





No electric field: mixing length > 5,000 μm Strong electric field (2 kV/mm) : mixing length < 150 μm





Electric Fields in Micro World

01 April 2013

M.Sc. Course on Process Intensification

16

(C. Tsouris, et al., AIChEJ, 49, 2181-2186 (2003))



Magnetic fields in chemical processing

Improving hydrodynamics in trickle-bed reactors

Mechanism:





01 April 2013

M.Sc. Course on Process Intensification



TUDelft

Iliuta et al., 2003; Munteanu et al., 2005



Comparison microwave heating vs. conventional heating







Inverted temperature gradients



Comparison microwave heating vs. conventional heating





Giving each molecule the same processing history



Microwave (MW) irradiation

Interaction with materials





www.cem.com



M.Sc. Course on Process Intensification





Mono-mode vs. Multi-mode devices

Mono-mode

- Standing waveform is created
- Vessel is placed in the dedicated singlemode position
- Heating performance for the reaction vial is easily predicted – uniform temperature distribution







Multi-mode

- Irradiation is dissipated in whole chamber through "wave stirrer"
- No specific position for sample
- Sample irradiated from every direction
- No limitations on the size and shape of the objects placed inside the cavity

01 April 2013

M.Sc. Course on Process Intensification



22

Microwaves in chemical synthesis



Monomode vs. Multimode Microwave Irradiation

	Microwave R-220A (Sharp)	Synthewave 402 (Prolabo)	ETHOS MR (MLS)
Microwave mode	multimode	monomode	multimode
Microwave power	800 W, pulsed	300 W, unpulsed	1000 W pulsed/ unpulsed
Volume of cavity	15.7 L	< 0.25 L	42.8 L
Power density	approx. 50 W/L	> 1200 W/L	approx. 23 W/L
Reaction scale	< 100 g (dry reactions)	< 100 g	up to 3000 g (depending on reactor type)

01 April 2013

M.Sc. Course on Process Intensification



(M. Nüchter, et al., Chem. Eng. Technol., 2003, 26, 1207)



Limitations of common microwave equipment



- Unpredictable and uncontrollable microwave and temperature fields
- Difficult to rationalize the results
- Difficult to optimize the process and harness the intensification potential of microwaves



Limitations of common microwave equipment





Vertical temperature distribution along the center line for Rh/CeO₂-ZrO₂ catalyst





26

Horizontal temperature distribution at a fixed position





New microwave heating system with

Internal transmission line technology



M.Sc. Course on Process Intensification

http://www.sairem.com/gb/equipements/equipements_chimie/synthese_sous_micro_ondes.html WO 2009/122101 Device for applying electromagnetic energy to a reactive medium



Industrial multimode furnaces (drying)





01 April 2013

M.Sc. Course on Process Intensification





Microwave Energy Versus Other Electromagnetic Energy



Radiation Type	Typical Frequency (MHz)	Quantum Energy (kcal/mol)	Chemical Bond Type	Chemical Bond Energy (kcal/mol)
Gamma Rays	3.0 x 10 ¹⁴	2.86 x 10 ⁷	H-OH	120
X-Rays	3.0 x 10 ¹³	2.86 x 10 ⁶	H-CH ₃	104
Ultraviolet	1.0 x 10 ⁹	95	H-NHCH ₃	92
Visible Light	6.0 x 10 ⁸	58	H ₃ C - CH ₃	88
Infrared Light	3.0 x 10 ⁶	0.28	PhCH ₂ -COOH	55
Microwaves	2450	0.037	H, HO, H	4.8
Radio	1	9 x 10 ⁻⁸	Ю́ Н	

01 April 2013	M.Sc. Course on Process Intensification		30
Courtes: CEM Corporation, 2005		(F	





Some examples:



	Reaction time		Product Yield	
Reaction	Conventional	Microwave	Conventional	Microwave
Hydrolysis of benzamide to benzoic acid	1 h	10 min	90%	99%
Oxidation of toluene to benzoic acid	25 min	5 min	40%	40%
Esterification of benzoic acid with methanol	8 h	5 min	74%	76%
S _N 2 reaction of 4- cyanophenoxide ion with benzyl chloride	16 h	4 min	89%	93%
Heck arylation of olefines	20 h	3 min	68%	68%



Microwave effects: why are (some) reactions sped up?

Thermal effects

- Superheating of polar solvents
- Superheating of catalysts
- Hot spots at molecular scale

Non-thermal effects (speculative)

- Orientation/alignment of molecules in a way that the frequency of effective collisions increases
- Decrease in activation energy due to increase in entropy owing to enhanced molecular motion (ΔE= ΔH-TΔS)



Mingos, D. M. Superheating Effects Associated with Microwave Dielectric Heating. *J. Chem. Soc. Chem, Commun.* 1992, *6*, 674

M.Sc. Course on Process Intensification





(R. Jachuck, et al., Green Chem., 8, 29-33 (2005))



Direct polyesterification (butane-1,4-diol with succinic acid) catalyst, 200°C OH. OH + HO HO Poly (butylene succinate) (PBS) **PRODUCT PROPERTIES NOT** 1.8 **ACHIEVABLE WITH** microwave heating \diamond 1.5 **CONVENTIONAL TECHNOLOGY** conventional heating 10^{4} 1.2 × 0.9 ≥ ∑ Resulting molecular weight increase by 1,6 fold & rate of polymerization increase 0.6 by 10 fold 0.3 0 0 30 60 90 120 150 180 210 240 270 300 330 16323 time [min] diamon and a state



Polymerization of polystyrene



PRODUCT PROPERTIES NOT ACHIEVABLE WITH CONVENTIONAL TECHNOLOGY

Microwave reactor

Conventional reactor





35

Microwaves in heterogeneous catalysis

Selective heating of catalytic sites with MW





Virginia Polytechnic and State University – **Simulation of MW heating of metallic catalyst on alumina support** (J. R. Thomas, Catal. Lett., 49, 137-141 (1997)) Imperial College - MW heating of molybdenum catalyst on alumina support (X. Zhang et al., Ind. Eng. Chem. Res., 40, 2810-2817 (2001))



M.Sc. Course on Process Intensification



36



Microwave – activated methanol steam reforming

Durka, T. et. al., Int. J. Hydrogen. Energy, 2011, 36, p. 12843



Microwave-activated methanol steam reforming



M.Sc. Course on Process Intensification

Durka, T. et. al., Int. J. Hydrogen. Energy, 2011, 36, p. 12843



Energy efficiency of the reactor



Durka, T. et. al., Int. J. Hydrogen. Energy, 2011, 36, p. 12843



MW-assisted regeneration of adsorbents

Investigated system:

- <u>Adsorbate</u>: polar compound (acetone) / non-polar (toluene)
- <u>Adsorbent</u>: synthetic zeolites (type 13X)

Comparison of two types of regeneration:

- <u>Temperature Swing Regeneration (TSR)</u> purge gas stream heated conventionally in a coil pipe
- <u>Microwave Swing Regeneration (MSR)</u> cold inert gas stream; zeolite beads are heated by MW



Cherbanski, R. *et. al.*, Microwave Swing Regeneration vs Temperature Swing Regeneration, *Ind. Eng. Chem. Res.*, 2011, 50, p. 8632



MW-assisted regeneration of adsorbents



M.Sc. Course on Process Intensification

Cherbanski, R. *et. al.*, Microwave Swing Regeneration vs Temperature Swing Regeneration, *Ind. Eng. Chem. Res.*, 2011, 50, p. 8632



MW-assisted regeneration of adsorbents



M.Sc. Course on Process Intensification

Cherbanski, R. *et. al.*, Microwave Swing Regeneration vs Temperature Swing Regeneration, *Ind. Eng. Chem. Res.*, 2011, 50, p. 8632



MW-assisted regeneration of adsorbents: desorption efficiencies





Advantages of microwave heating

Fast heating

- Flexible throughputs
- Desirable in particular processes (e.g., production of toxic chemicals, regeneration of Diesel particulate filters)
- Higher chemical selectivity

Selective heating

- Potential for better energy utilization efficiency in processes involving (gas-solid, liquid-solid) interphases (e.g. low temperature synthesis, specific desorption)
- Safer operation
- Higher chemical selectivity due to suppression of bulk reactions

No heat exchange surfaces

• Reduce fouling of equipment surfaces

Main barrier: Scale-Up

M.Sc. Course on Process Intensification





Microwaves in chemical processing – efficiency issue





Why microwaves?

Electricity: today more expensive than gas

MW heating more expensive than steam heating







45

Microwaves in chemical processing – efficiency issue

Why microwaves?

Electricity: in the post-oil age the widest available, sustainable form of energy.



Water and effluent treatment

· destruction of contaminants in water

Polymer chemistry

- · degradation of polymer compounds
- initiation of polymerization reactions

Sono-electrochemistry (ultrasound with electrolysis)

- lowering cell voltages
- minimization of electrode fouling

Textile industry

- · dispersion and break-up of dye aggregates
- expulsion of entrapped air from fibre capillaries

In chemical reactions: Reduction in reaction time Increase in the yield Switching of the reaction pathway Changing the product distribution



01 April 2013

M.Sc. Course on Process Intensification



47



(P. R. Gogate, et al., 2004)





(K. Yasui, at al., Ultrasonics Sonochemistry, 2005, 12, 43-51)



Solid-liquid mass transfer enhancement







Solid-liquid mass transfer enhancement



intensified by hydromechanical effects of ultrasound. Frequency 3217 kHz, sample volume 250 ml.



Gas-liquid mass transfer enhancement



Mature



Ultrasound effects on reactions

Depation	Reaction time		Product Yield	
Keaction	Conventional	Ultrasound	Conventional	Ultrasound
Diels-Adler cyclization (hom.)	35 h	3.5 h	77.9%	97.3%
Oxidation of indane to indan-1-one (hom.)	3 h	3 h	< 27%	73%
Reduction of methoxyaminosilane (het.)	no reaction	3 h	0%	100%
Epoxidation of long-chain unsaturated fatty esters (het.)	2 h	15 min	48%	92%
Oxidation of arylalkanes (het.)	4 h	4 h	12%	80%
Michael addition of nitroalkanes to monosubstituted α , β -unsaturated esters (het.)	2 days	2 h	85%	90%
Permanganate oxidation of 2-octanol (het.)	5 h	5 h	3%	93%
Synthesis of chalcones by Claisen- Schmidt condensation (het.)	60 min	10 min	5%	76%
Ullmann coupling of 2-iodonitrobenzene (het.)	2 h	2 h	< 1.5%	70.4%
Reformatsky reaction (het.)	12h	30 min	50%	98%

01 April 2013

M.Sc. Course on Process Intensification

53

(L. H. Thompson, L. K. Doraiswamy, Ind. Eng. Chem. Res., 1999, 38, 1215-1249)



Sonochemical reactors

Embryonic Growth Mature Aging

Stirred-tank configuration



01 April 2013

M.Sc. Course on Process Intensification



(L. H. Thompson, L. K. Doraiswamy, Ind. Eng. Chem. Res., 1999, 38, 1215-1249)





(L. H. Thompson, L. K. Doraiswamy, Ind. Eng. Chem. Res., 1999, 38, 1215-1249)



Application barriers:

- scale-up methodology
- large-scale efficiency





M.Sc. Course on Process Intensification



56

(L. H. Thompson, L. K. Doraiswamy, Ind. Eng. Chem. Res., 1999, 38, 1215-1249)





Scale up: limited penetration depth





Other methods for cavitation forming

Liquid Whistle

- liquid flows across a vibrating plate
- frequency of vibrations adjusted to create cavitation
- large liquid volumes can be processed
- presence of solids can cause blade erosion





Embryonic Growth Mature Aging

Other methods for cavitation forming

Hydrodynamic cavitation



- Can be generated by the passage of the liquid through a constriction, such as throttling valve, orifice plate, venturi etc.
- If the pressure in *vena contracta* falls below the cavitation pressure (usually vapour pressure of the medium), millions of cavities are generated
- When liquid jet expands and pressure recovers, the cavities collapse





59

Other methods for cavitation forming



Hydrodynamic cavitation – alternative to ultrasound

No.	Reactants	Product ^e	Cavitational yield in hydrodynamic cavitation reactor (gm/J)	Cavitational yield in acoustic cavitation reactor (gm/J)
1	Toluene	Benzoic acid	3.3×10 ⁻⁶	5.6×10 ⁻⁷
2	p-Xylene	Terephthalic acid	2.1×10^{-6}	3×10 ⁻⁷
3	o-Xylene	Phthalic acid	1.9×10^{-6}	3×10 ⁻⁷
4	m-Xylene ^d	Isophthalic acid	1.9×10^{-6}	_
5	Mesitylene	Trimesic acid	7×10 ⁻⁶	1×10^{-7}
6	o-Nitrotoluene	o-Nitrobenzoic acid	1.9×10^{-6}	1×10 ⁻⁷
7	m-Nitrotoluene	m-Nitrobenzoic acid	1.3×10^{-6}	1×10^{-7}
8	p-Nitrotoluene ^e	p-Nitrobenzoic acid	_	3×10 ⁻⁷
9	o-Chlorotoluene	o-Chlorobenzoic acid	1.1×10^{-6}	1×10^{-7}
10	p-Chlorotoluenef	p-Chlorobenzoic acid	2×10^{-6}	_
11	Sunflower oil	Bio-diesel (methyl ester of sunflower oil)	$2.1 \times 10^{-6^{*}}$	$5.1 \times 10^{-7^{+}}$

Comparative results for different industrially important reactions in hydrodynamic^a and acoustic^b cavitation reactors

*In moles/J.

01 April 2013 60 M.Sc. Course on Process Intensification (P. R. Gogate, A. B. Pandit, Ultrasonic Sonochemistry, 2005, 12, 21-27)



Energy of flow - supersonic shockwave

- 1995 Mattick *et al.* described a supersonic shockwave reactor for pyrolysis of hydrocarbons ethylene yield in increased by 20% as compared to conventional technology, while the energy consumption dropped by 15%.
- **1997** Praxair presents a supersonic gas-liquid reactor for carrying-out fast processes oxygen transfer rate in water is up to ca. 10 times higher than in a tee-mixer. Mass transfer coefficients exceeding 2.0 s-1 are reported.
- **1998** Messer Griesheim GmbH commercializes a supersonic nozzle for fluidized-bed applications:
 - iron sulfate decomposition at Bayer AG: capacity of the reactor increased by 124%.
 - sludge combustion reactors: throughput increased by approximately 40%





Energy of flow - supersonic shockwave





2003:Transonic oxygen injection at DSM - fermentation capacity doubled



M.Sc. Course on Process Intensification

01 April 2013

62

