REVIEW PAPER

ENERGY MATTERS
Alternative Sources and Forms of Energy for Intensification of Chemical and Biochemical Processes

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This paper brings a review of the alternative sources and forms of energy that can be utilized in order to achieve drastic improvements in the efficiency of chemical and biochemical processes (process intensification). Literature data on achievable intensification effects are provided. Also, some alternative ways of introducing energy in the chemical process equipment are presented. Although the process intensification potential of many of those alternative sources and forms of energy has already been proven in the laboratories, their application on the industrial scale still presents a formidable challenge for the chemical engineering community. In the paper the most important design and scale-up problems in those novel technologies are discussed and recommendations are given regarding the future research activities. To achieve radical progress in this area more research effort on the interface between the chemical engineering, chemistry, material science and applied physics is needed.

Keywords: process intensification; high-gravity; microwaves; photochemistry; cavitation; supersonic flow.

INTRODUCTION

The world's consumption of non-renewable resources by the chemical and related industries is rapidly increasing, as new types of chemical and biochemical products are brought each year to the market and new markets open in different parts of the world for already existing products. The rapid growth in world's population accompanied by general growth in human wealth and the growth in consumers' needs are the most important reasons of the increased consumption of chemical and biochemical products. This situation is not sustainable. Many credible sources predict that still in the 21st century the human race will face a dramatic decrease of the oil production. Other non-renewable resources, such as natural gas or noble metals, sooner or later will follow the same path. On the other hand, the average efficiency at which resources are converted into the final products is still dramatically low. Experts claim that in order to achieve a 'steady-state' and retain the Earth's ecosphere in its present shape the resource efficiency of production processes has to increase by a factor of four

(Von Weizsacker, 1998) or even 10 (Schmidt-Bleek, 1993). Accordingly, the sustainability-oriented research in the chemical and biochemical engineering in the coming decennia will need to focus on

- development of *technically and economically feasible* processes based on the *renewable feedstocks* (biomass-based processes);
- development of innovative methods and technologies that would drastically *increase the efficiency of chemical and biochemical manufacturing*.

The latter presents the main goal of Process Intensification.

Different alternative sources and forms of energy can be applied in order to intensify a chemical or biochemical process. The most important include

- energy of high-gravity fields;
- energy of electric fields—stationary and dynamic;
- energy of electromagnetic radiation—microwaves and light;
- energy of acoustic fields;
- energy of flow.

The present paper reviews and critically examines those alternative sources and forms of energy, as potential means for process intensification.

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ENERGY OF HIGH-GRAVITY FIELDS

The use of high-gravity fields generated by the centrifugal operation dates actually to the beginning of the industry with such physical transport operations as pumping, compression and solid–liquid separations. An important milestone of liquid–liquid contacting in the centrifugal equipment was the application of the Podbielniak extractor to the recovery of penicilin (Podbielniak *et al.*, 1970). The use of high-gravity fields for process intensification starts with the pioneering work of Ramshaw and Mallison from the ICI New Science Group who carried out studies on the application of high-gravity fields (so-called 'HiGee') in distillation processes (Ramshaw and Mallison, 1981; Ramshaw, 1983). The patent by Ramshaw and Mallison (1981) describes a distillation process in a rotating packed bed (RPB) and reports a 27 to 44-fold increase of the liquid-side mass transfer coefficient and four to nine-fold increase of the gas-side mass transfer coefficient, with respect to the stationary bed of $\frac{1}{2}''$ Intalox saddles. Other authors have later confirmed such a large increase in the mass transfer rates in the high-gravity field of the rotating packed bed. Chong Zheng and co-workers investigated hydrodynamics and heat transfer in a cross-flow RPB and found the height of the mass transfer unit for the liquid-side controlling processes as low as 2.5–4 cm (Guo *et al.*, 1997). Lin and co-workers investigated the methanol–ethanol distillation process in a rotating packed bed and reported the HETP (height equivalent of theoretical plate) values of 3–9 cm, compared to 30–40 cm for the conventional structured packings (Lin *et al.*, 2002). Also, the data provided in the review paper by Rao and co-workers indicate that up to ca. 200 times increase of the $k_L a$ in the RPBs with respect to the conventional packed columns is possible (Rao *et al.*, 2004). Such excellent mass-transfer properties of the RPBs have led to a number of commercial applications. RPBs have been applied to the water deaeration in oil fields in China (Zheng *et al.*, 1997). Table 1 shows the comparison between the conventional technology for water deaeration (vacuum desorption tower) and the HiGee technology designed for the off-shore application. High gravity technology has also been commercially applied in Dow's hypochlorous acid process (Trent, 2004). Other interesting examples of investigated applications of RPBs include production of nanoparticles (Chen *et al.*, 1997) and ozone oxidation processes (Lin and Liu, 2003).

The spinning disc reactor (SDR), developed by Ramshaw and co-workers at the University of Newcastle

(Ramshaw, 2004), presents the second important type of device using the energy of high-gravity fields. Here, the rotating surface of the disc enables to generate a highly sheared liquid film. The film flow over the surface is intrinsically unstable and an array of spiral ripples is formed. This provides an additional improvement in the mass and heat transfer performance of the device. The mass and heat transfer performance of the SDR is indeed impressive. Aoune and Ramshaw (1999) investigated the heat and mass transfer characteristics of liquid films on rotating discs and found local heat transfer coefficients ranging from ca. 10 000 to ca. 30 000 W m^{-2} K^{-1} (Figure 1) and local mass transfer coefficients between ca. 4E-04 and 1E-03 m s^{-1}, much higher than predicted by the Higbie model (Figure 2). The enhancement of the local mass transfer coefficients appears to be associated with the passage of the ripple, as highlighted in the experimental work by Brauner and Maron (1982). Excellent heat and mass transfer characteristics of the SDR have been confirmed by the study of a phase-transfer-catalysed Darzen's reaction for preparing a drug intermediate. The SDR allowed here for 99.9% reduction in reaction time, 99% reduction of inventory and 93% reduction of impurities level (Oxley *et al.*, 2000). Other possible applications of the SDR
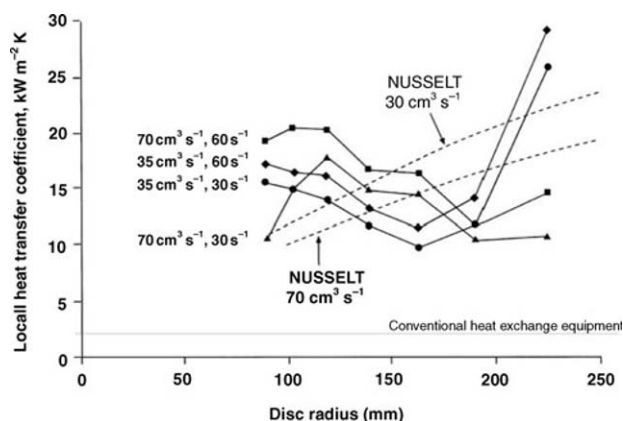

Figure 1. Local heat transfer coefficients in a spinning disc reactor at various water flow rates and rotational speeds (reprinted from Aoune and Ramshaw, 1999, with permission from Elsevier).
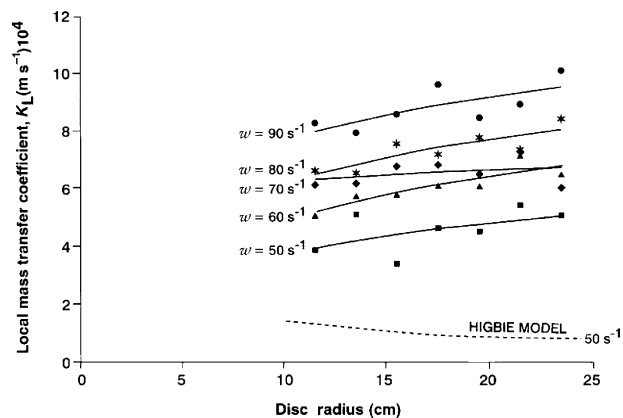

Figure 2. Local mass transfer coefficients in a spinning disc reactor at water flowrate of 80 cm^3 s^{-1} and various rotational speeds (reprinted from Aoune and Ramshaw, 1999, with permission from Elsevier).

Table 1. A comparison of Higrav deaerator with vacuum tower deaeration system for off-shore application (Zheng *et al.*, 1997).

	Vacuum tower (one set 10 000 t/d)	Higrav Deaerator (two sets 6000 t/d)
Platform area (m^2)	30	2 × 10
Height (m)	14	3
Weight (t)	60 (dry)	2 × 10 (dry)
	130 (operation)	2 × 10.5 (operation)
Residual oxygen (ppm)	1 (summer)	<0.05 (summer)
	2–3 (winter)	<0.05 (winter)
Investment	1	0.8
Power (kW)	155	2 × 160

investigated (Ramshaw, 2004) included polymerizations and polycondensations (in both cases considerable time savings and more uniform product) as well as precipitation/crystallization (smaller crystals with much narrower size distribution). In recent years two large chemical companies have patented processes based on the spinning-disc technology. SmithKline Beecham has claimed a method for epoxidising substituted cyclohexanones (Brechtels-Bauer and Oxley, 2001), while Procter and Gamble has patented a process for making esters and amides using the SDR (Burns et al., 2002).

A quite interesting recent application area for the high-gravity field-related technologies is the nuclear fuel reprocessing industry, where large remote handling operations are very capital intensive. Here, reduction of the equipment size, simpler design and better reliability can bring large returns on investment. Yarbro and Scheiber (2003) described the application of an annular centrifugal contactor to actinides purification at Los Alamos National Laboratory. The ratio between the flow rate of the processed liquids and the working volume of the apparatus was found for the ACC to be more than 16 times higher than for the packed column, 3.7 times higher than for a mixer–settler system and almost 1.4 times higher than for a pulsed sieve plate column.

ENERGY OF ELECTRIC FIELDS

The ability of superimposed electric fields, either static or dynamic, to improve chemical processes has been known for many years. The research focus in the past decennia was primarily on the applications of electric field in the separation processes and heat transfer operations. Mass transfer enhancement by the electric field in the liquid–liquid extraction has been investigated by numerous authors. Usually, enhancement factors between two and 10 are reported (Scott, 1989; Weatherley, 1992; Ptasinski and Kerkhof, 1992; He et al., 1993; Glitzenstein et al, 1995). Ptasinski and Kerkhof (1992) ascribe the observed mass transfer enhancement to a higher degree of turbulence within and around the dispersed phase, as a result of interaction between the field and the interface. Four different mechanisms are mentioned:

- higher terminal drop velocities resulting from electrical forces of attraction exerted on the drops in the direction of motion;

- generation of the electrically driven circulating flow in the neighbourhood of the interface;
- alteration of the velocity profiles within and around individual droplets due to the oscillations by pulsed electric fields;
- interfacial tension-induced surface flows (Marangoni effects) due to the presence of electric charges.

Scott (1989) describes the surface area formation via the electric-field-induced emulsification. Electric field applied to a nozzle results in a jetting phenomenon and the formation of an electrically charged emulsion of micron-sized droplets. The method may lead to a 200 to 500 times increase in the surface area per unit volume, compared to the millimeter-sized droplets in the conventional extraction processes.

Heat transfer can also be greatly influenced by application of an electric field. Kaji et al. (1980) observed ca. two to three-fold increase in the heat transfer coefficients from water droplets in silicone oil rising in the intermittent electric field. The heat transfer in boiling liquids was also reported to increase by a factor of four to 10 under the influence of alternating electric fields with low intensity (2 to 10 kV cm^{-1}) (Bochirol et al., 1962; Bonjour et al., 1962). Darabi et al. (1998) investigated heat transfer enhancement by the electric field in falling film evaporators. Up to a seven-fold enhancement of the heat transfer coefficient was documented.

The non-equilibrium cold plasma generation via the formation of high-pressure gliding electrical discharges (so-called GlidArc technology) presents another form of the energy of dynamic electric field used for chemical processing (Czernichowski, 1994; Fridman et al., 1999). In basic configuration diverging electrodes are placed in a fast gas flow, in the flow direction. Gliding discharges are produced between the electrodes and across the flow. The discharges start at the spot where the distance between the electrodes is the shortest and spread by gliding progressively along the electrodes in the direction of flow until they disappear at a certain distance (see Figure 3). In recent years many variants of the above basic configuration and alternative designs of the gliding-arc reactors have been studied (Dalaine et al., 1998; Meguernes et al., 2001; Krawczyk, 2002; Ruszniak et al., 2003; Yao et al., 2005; Kalra et al., 2005; Rusu et al., 2005; Młotek et al., 2005). The gliding arc technology could be utilized in numerous industrial applications, some of which have
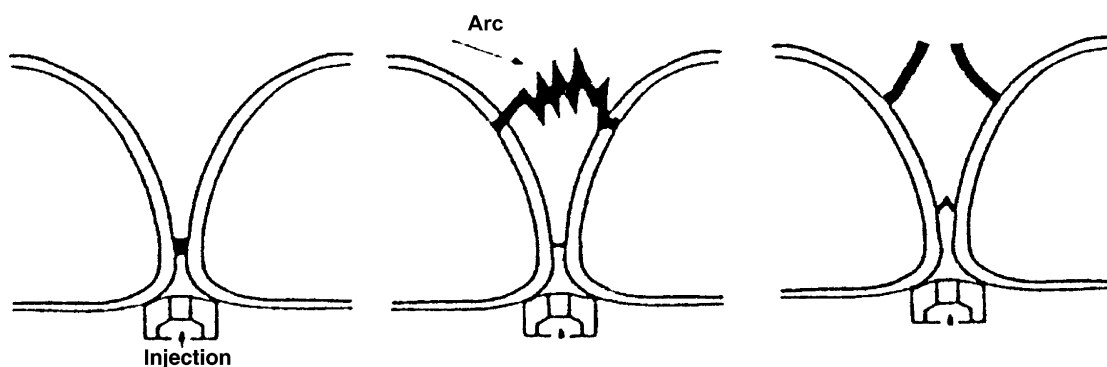

Figure 3. Basic configuration of the GlidArc device, showing start, life and disappearance of the gliding discharge (reprinted from Czernichowski, 1994, with permission from IUPAC).

already been tested both in the laboratory and on the pilot-scale. These applications include:

- emission control of industrial volatile organic compounds (VOC), ammonia, phenols, formaldehyde, H_2S, and so on;
- emission control of soot, (poly)aromatic hydrocarbons, SO_x and NO_x;
- complete or partial incineration of H_2S (also in combination with CO_2);
- production of syngas from natural gas or other carbonaceous feedstocks (e.g., propane);
- methane conversion to acetylene and hydrogen;
- oxydation of methanol to formaldehyde;
- destruction of N_2O;
- reforming of heavy petroleum residues;
- destruction of concentrated freons;
- CO_2 dissociation;
- overheating of steam, oxygen or other gases;
- ignition of propellants;
- UV generation;
- decontamination of soil or industrial sands;
- activation of organic fibres.

The information about possible process intensification-effects of gliding arc technology is limited. Definitely, the most significant improvement with respect to conventional processes can be expected in the energy efficiency. Up to 45% of electrical energy can be absorbed directly in the endothermic reaction (Czernichowski, 1994). Meguernes et al. (2001) report output energy efficiencies of 27–30% for methane conversion with carbon dioxide to synthesis gas at conversion rates exceeding 90%. Czernichowski et al. (2003) report consumption of only 100 W of electrical energy to produce 3 Nm^3 h^{-1} of pure syngas from propane, corresponding to about 10 kW of electrical power of an ideal fuel cell. Propane was totally reformed at more than 70% energetic efficiency and at the total absence of soot. Activating the chemical reactions by electrical discharges can furthermore allow replacing some conventionally catalytic processes by non-catalytic ones. Minimization of the equipment size and weight presents another possible PI-effect of the GlidArc technology (Czernichowski, 2001), although comparative studies are needed in order to come to a quantitative appraisal.

ENERGY OF ELECTROMAGNETIC RADIATION: THE MICROWAVES

Microwave-assisted operations present undoubtedly a very promising type of electromagnetic field application to intensify chemical processes. *Microwave (dielectric) heating* of materials has been known for a long time and development of microwave ovens has more than 50 years of history. The classical publication by Gedye et al. (1986) has opened a period of very intensive investigations of the microwaves effect on chemical reactions.

In general, microwave frequencies range from 0.3 to 300 GHz, which corresponds to the wavelength between approximately 1 mm and 1 m. Much part of this range is occupied by the radar and telecommunication applications and in order to avoid interference the industrial and domestic microwave appliances operate at several standard allocated frequencies, most often at 2.45 GHz. Molecules that have a permanent dipole moment (e.g., water) can rotate in a fast changing field of microwave radiation. As a result of that rotation an 'internal friction' occurs in the polar medium, which is heated directly and almost evenly. The magnitude of this effect depends on dielectric properties of the substance to be heated.

The literature concerning the enhancement effects of the microwaves on chemical reactions, homogeneous liquid-phase organic reactions in particular, is exceptionally rich. Since the original articles of Gedye et al. (1988) hundreds of research papers have been published and there exist several good reviews on this subject (Lidström et al., 2001; Hayes, 2002; Hájek, 2002; Larhed et al., 2002; Kappe, 2004). Authors generally agree about the ability of microwave heating to accelerate organic reactions and acceleration factors from several to more than a thousand are reported. Several examples of reactions accelerated by the microwave heating are given in Table 2. One can see that not only the rate of the process is affected, but also the product yield, which in some cases increases as a result of microwave heating.

The discussion about how the highly polarizing radiation of microwaves promotes and accelerates chemical reactions is still going on. Microscopic hot-spots, molecular agitation and improved transport properties of molecules have been mentioned as potential mechanisms of activation (Jacob et al., 1995). Other hypothetic effects, such as positioning of the transitions states or decrease of the activation energy in Arrhenius law were also postulated and discussed (Howarth and Lockwood, 2004). Recently more and more authors agree that the effect of microwaves has a purely thermal character (Lidström et al., 2001; Kuhnert, 2002; Kappe, 2004), although for others this appears still a too simplistic explanation (Perreux and Loupy, 2001, 2002; De la Hoz et al., 2004).

Dramatic effects of microwave irradiation have also been reported for solvent-free synthesis systems (Loupy et al., 1998) and in heterogeneous catalysis (Bond et al., 1993; Will et al., 2004). For example, Zhang et al. (2003) investigated microwave-assisted oxidative coupling of methane on alumina supported La_2O_3/CeO_2 catalyst and observed

Table 2. Effect of microwave heating on reaction time and product yield for several exemplary reactions (after: Gedye et al., 1988; Larhed et al., 2002).

| Reaction	Reaction time		Product yield	
	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_N2 reaction of 4-cyanophenoxide ion with benzyl chloride	16 h	4 min	89%	93%
Heck arylation of olefines	20 h	3 min	68%	68%
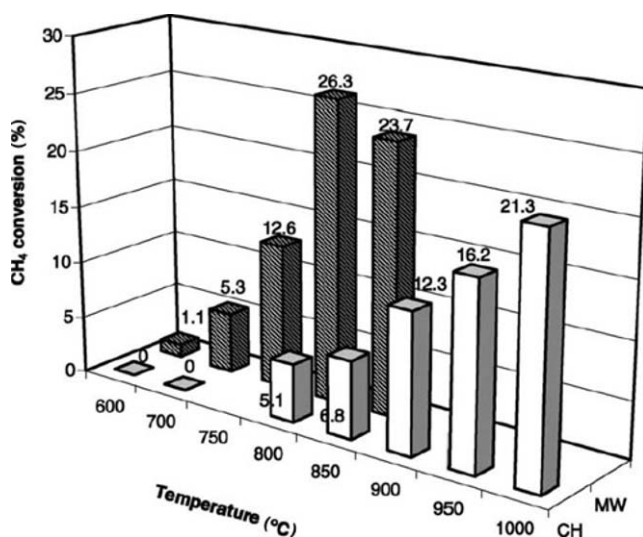
Figure 4. Effect of microwave irradiation on methane conversion to C$_2$ hydrocarbons in the absence of oxygen (MW: microwave heating; CH: conventional heating) (reprinted from Zhang *et al.*, 2003, with permission from Elsevier).

that in the absence of oxygen conversion into the C$_2$ products occurred at temperatures about 250°C lower than during the conventional heating (Figure 4). The authors ascribed this dramatic effect to the CH$_4$ plasma formation and arcing.

Despite obvious intensification effects of the microwave irradiation on chemical reactions and other advantages such as energy savings, mild treatment in case of temperature-sensitive systems or absence of fouling, as yet no industrial microwave-assisted process has been reported. The recent paper by Nüchter *et al.* (2004) brings a good critical overview of the current situation in the technology of microwave-assisted synthesis. One of the main barriers for industrial applications is reliable scale-up of microwave reactors. Since vast majority of the papers in the field have been published by organic chemists and physicists, little attention has been given so far to the engineering aspects of large-scale microwave reactors. Small penetration depth of microwaves (ca. 1.4 cm in water at 25°C) poses definitely a certain problem here but in view of the short reaction times offered by the microwave heating possible solutions should be sought in the continuous rather than the batch processing. First studies of a pilot-scale continuous microwave reactor for dry-media reactions have already been reported (Esveld *et al.*, 2000a, b). Along with reactions also distillation systems could possibly benefit from the continuous microwave equipment. Microwave irradiation was found to be able to speed-up the batch distillation processes up to 20 times (Armstrong and Neas, 1990). Several concepts of microwave-driven distillation equipment have been developed and patented (Rajamannan, 1981; Armstrong, 1995).

ENERGY OF ELECTROMAGNETIC RADIATION: THE LIGHT

Using light in chemical processing has a long history. First industrial technologies using light to induce

chain reactions (photochlorinations) have been developed before WWII. Photopolymerizations, photonitrosylations of alkanes or photosynthesis of previtamin D are well-known examples of the commercial-scale applications. Every year hundreds of new research papers appear describing various aspects of *photocatalytic processes.* From the process intensification viewpoint, the use of light, either artificial or solar, for carrying out chemical and biochemical reactions may result in two sustainability-related effects:

● drastic increase of process selectivity to the required products (e.g., due to a different chemistry, or low/ambient process temperature);
● drastic decrease of the (non-renewable) energy consumption in the process (e.g., due to the low-temperature processing or use of solar light).

An excellent example of how light can drastically improve the selectivity of industrially relevant chemical reactions, are the studies carried out in the group of Frei at Berkeley University (Sun *et al.*, 1994, 1996a, b; Blatter *et al.*, 1998; Kirkby and Frei, 1998). Oxidations of small hydrocarbons, carried out with visible light on various types of zeolites resulted in exceptionally high reaction selectivities. For instance, complete (100%) selectivity was reported for toluene oxidation to benzaldehyde on CaY zeolite (Sun *et al.*, 1994) and cyclohexane oxidation to cyclohexanone on NaY zeolite (Sun *et al.*, 1996a). Selectivities remained high even upon more that 50% conversion of the hydrocarbon loaded into the zeolite matrix. Relatively high were also quantum efficiencies of the processes studied, in average between 10 and 30% (Sun *et al.*, 1996b).

Another area where light can be used to enhance the reaction selectivity, is the field of asymmetric (chiral) synthesis. This area is of particular interest and importance to the pharmaceutical industry. The fact that (circularly polarized) light can be used to obtain selectively the required enantiomer from a non-chiral starting material has been confirmed by many authors. Enantioselective photoreactions can be carried out both in solutions and in the solid state, and there are several good literature reviews on this subject (Inoue, 1992; Everitt and Inoue, 1999; Feringa and Van Delden, 1999; Toda *et al.*, 2001).

A step further in the area of photocatalysis is to replace the artificial light by the concentrated sunlight, thus approaching the ideal of a 'green' process. Some possibilities here (up to the pilot-plant scale) were demonstrated not only for TiO$_2$-based water treatment applications (Malato *et al.*, 2002; Bahnemann, 2004; Kabra *et al.*, 2004), but also for chemical production, in particular of fine chemicals (Esser *et al.*, 1994; Pohlmann *et al.*, 1997; Schiel *et al.*, 2001).

The primary engineering challenge (also from the process intensification viewpoint) in the field of photocatalysis for chemical manufacturing is the development of a technically and economically feasible photoreactor. Numerous designs of (catalytic) photoreactors have been proposed so far, including coated fluorescent tubes, fluidized-bed designs, falling-film designs and hollow-tube or optical-fibre-based reactors (see review by Mills and Lee, 2004). However, the light efficiency (ratio between the light flux emitted and light flux reaching the catalyst) of most designs, in particular in (gas–)liquid–solid applications

remains still insufficient to make these reactors feasible from the energy-cost viewpoint. Also, the low catalyst area-to-reaction volume ratio presents a clear drawback of many proposed solutions. As a result, in photocatalytic wastewater treatment only a handful of reactor designs are offered commercially nowadays (Mills and Lee, 2004). New interesting developments in the field include an optical fiber monolith photoreactor (Lin and Valsaraj, 2005) and an ultraviolet LED photoreactor (Chen *et al.*, 2005).

ENERGY OF SOUND

Similarly to photochemistry, the research of the acoustic energy effects in the chemical processing has a long history and ultrasonic devices have already found a number of commercial applications, e.g., in cleaning and decontamination or in the textile industry (dye dispersion and fixation). First reports on chemical and biological rate enhancement by the ultrasound were published in the late 1920s. Since early 1980s the field of sonochemistry has become a very popular area of (mostly) chemical research. The main focus of that research is on the liquid-phase systems, where exposure to ultrasound results in formation, growth and subsequent collapse of microbubbles (microcavities), occurring in the extremely short period of time (milliseconds). The microimplosions are accompanied by an energy release with very high energy densities (order of up to 10^{18} kW m^{-3}), which leads to local generation of extremely high temperatures and pressures, up to ca. 5000 K and ca. 50 000 bar, respectively, as well as release of free radicals due to pyrolysis of water (Gogate *et al.*, 2003a, b). Similarly to microwaves, the use of ultrasound can dramatically speed-up chemical reactions and increase the product yield. Some examples of such ultrasound effects, both in homogeneous and in heterogeneous reaction systems, are shown in Table 3. More data can be found in the excellent review paper by Thompson and Doraiswamy (1999). Acoustic irradiation appears to be able not only to boost chemical reactions, but also to intensify mass transfer processes in multiphase systems. Kumar *et al.* (2004) investigated gas–liquid mass transfer coefficients in sparged sonochemical reactors and observed a circa two-fold increase of k_La when ultrasound was used. The effect was even stronger (up to five times increase) when NaCl (electrolyte) was added to the system. Other factors influencing that effect included gas flow rate, power dissipation rate and (in particular) the position of the gas sparger with respect to the ultrasonic transducer. Neis (2002) investigated the influence of the ultrasound in high frequency range (3217 kHz) on the liquid–solid mass transfer, by studying the solubilization rates of phenantrene and solid naphthalene. Up to 20-fold increase of the mass transfer coefficient was observed in both systems. A reduction of the boundary layer thickness due to the micro-scale turbulence and reduction of the viscosity in the boundary layer were postulated as the mechanism behind the observed phenomenon.

Lower acoustic frequencies can also be used to intensify transport processes. Already in 1957 Hodgins *et al.* studied the effects of sonic energy at frequencies between 100 and 700 Hz on the gas–solid mass transfer and found the enhancement of up to about 120% for the bed of spheres and up to about 220% for a single sphere. More recently,

Table 3. Effect of ultrasound on reaction time and product yield for several exemplary reactions (after: Thompson and Doraiswamy, 1999).

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

Krishna and Ellenberger (2002) used low-frequency (50–200 Hz) vibrations to improve performance of a bubble column and observed 50–100% increase of the volumetric mass transfer coefficient, depending on the flow rate.

Despite obvious process intensification effects of acoustic cavitation and numerous advantages of the sonochemical reactors, there is no industrial process known so far using this technology on the large scale. The reasons here are similar to those mentioned earlier when discussing the microwave-assisted processing. Despite many valuable papers on sonochemical reactor scale-up and design published in the recent years (Martin and Ward, 1992; Horst and Hoffmann, 1999; Keil and Swamy, 1999; Russel and Smith, 1999; Thompson and Doraiswamy, 1999; Horst *et al.*, 2002; Gogate *et al.*, 2003a; Gogate and Pandit, 2004a; Prabhu *et al.*, 2004), the proposed solutions are either not reliable enough or not economically feasible to apply them on the large-scale. The challenge for the chemical engineering research in this area for the coming years includes among other things a better understanding of the relation between a cavitation collapse and chemical reactivity, better understanding of the influence of various operational and design parameters on the cavitation process, development of reliable mathematical models and scale-up procedures, as well as solving some specific design problems like small penetration depth of acoustic waves, equipment erosion due to cavitation, and so on.

ENERGY OF FLOW

Similarly to ultrasound, the energy of liquid flow can be utilized to purposefully create cavitation for intensifying reactions and other operations. Such a purposeful hydrodynamic cavitation can be created on two ways. One

alternative is to let the liquid pass through a throttling valve, orifice plate or any other mechanical constriction [Figure 5(a)]. If the pressure in *vena contracta* falls below the cavitation pressure (usually the vapour pressure of the medium), millions of microcavities will be generated. Those cavities will subsequently collapse as the liquid jet expands and pressure recovers. Another possibility to create cavitation is to use the so-called *liquid whistle* [Figure 5(b)], already applied in food industry for homogenization and emulsification (Mason *et al.*, 1996). The characteristic feature of it is that the power here is transmitted from the medium to the device and not the other way round. The liquid is accelerated in a jet and then flows across a steel blade, which vibrates as liquid passes over it at high velocity. The frequency of those vibrations can be adjusted in such a way that cavitation is created. This way large liquid volumes could in principle be processed. Liquid whistle, however, suffers from several important shortcomings, such as very low vibrational power, low intensity of cavitation generated, high pumping costs and erosion of the blade in the presence of particulate matters (Gogate and Pandit, 2001).

Hydrodynamic cavitation reactors have been investigated for more than a decade now in the UDCT Department of Bombay University (Pandit and Moholkar, 1996; Moholkar *et al.*, 1999; Gogate and Pandit, 2001, 2005). When applied to some industrially relevant reactions, the hydrodynamically created cavitation appeared to deliver in average an order of magnitude higher cavitation yields than the acoustic cavitation (see Table 4). In addition, the processing volumes could be up to circa 100 times larger than in the conventional sonochemical reactors. So far, there is no information about the industrial applications of the hydrodynamic cavitation reactors, although some concepts have already been patented (Kozyuk, 1998).
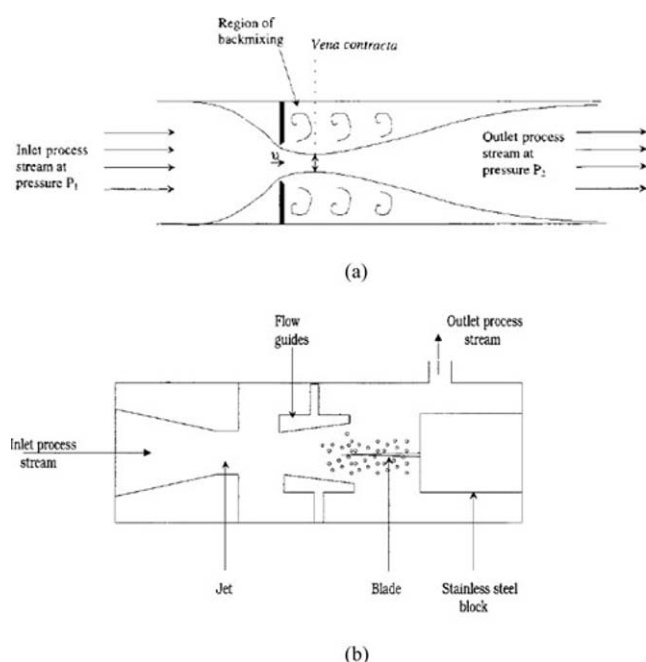

Figure 5. Creating cavitation in an orifice (a) or in a liquid whistle (b) (reprinted from Thompson and Doraiswamy, 1999, with permission from ACS).

Table 4. Hydrodynamic and acoustic cavitation yields for exemplary reactions (after: Gogate and Pandit, 2005).

Reaction	Cavitation yield (gm J^{-1})	
	Hydrodynamic	Acoustic
Toluene to benzoic acid	3.3×10^{-6}	5.6×10^{-7}
p-Xylene to terephthalic acid	2.1×10^{-6}	3×10^{-7}
m-Xylene to isophthalic acid	1.9×10^{-6}	3×10^{-7}
o-Nitrotoluene to o-nitrobenzoic acid	1.9×10^{-6}	1×10^{-7}
o-Chlorotoluene to o-chlorobenzoic acid	1.1×10^{-6}	1×10^{-7}

Using the energy of the supersonic shockwave presents another promising alternative method for intensification of the phase contacting and transport processes. In 1995 Mattick *et al.* described a supersonic shockwave reactor for pyrolysis of hydrocarbons, in which a gas cooled to sub-pyrolysis temperature by expansion to supersonic speed was mixed with a supersonic flow of feedstock. The ethylene yield in such a reactor increased by 20% as compared to conventional technology, while the energy consumption dropped by 15%. Interestingly, most research in the field of supersonic chemical processing has been carried out in industrial environment and led to a number of commercial applications. For example, Praxair investigated a supersonic gas–liquid reactor for carrying-out fast processes (Cheng, 1997, 1999) The energy of the supersonic shockwave is used here to disperse gas into tiny microbubbles and by that to create an enhanced interfacial area for mass transfer. Results of experiments carried out with oxygen–water system show that the oxygen transfer rate in a supersonic reactor is up to ca. 10 times higher than in a tee-mixer. Mass transfer coefficients exceeding 2.0 s^{-1} are reported (Cheng, 1997). German company Messer Griesheim GmbH has patented and commercialized a supersonic nozzle for fluidized-bed applications (Gross, 1998a, b). The concept was subsequently applied on the industrial scale in a fluidized-bed reactor for iron sulfate decomposition at Bayer AG. Supersonic injection of oxygen has increased the capacity of the reactor by 124% (Gross, 2000). The same technology has also been applied to the sludge combustion reactors increasing the throughput by approximately 40% (Gross and Ludwig, 2003). Recently, DSM reported development and application of a supersonic oxygen injection technology in one of their large-scale fermentation processes. New type of the supersonic injection system has doubled the yeast productivity of the fermenter (Groen *et al.*, 2005). These several industrial applications reported in the literature prove that the energy of supersonic flow can be successfully used as a tool to enhance the interfacial contacting and intensify mass transfer processes in multiphase systems. However, more interest from academia and more generic research activities are needed in this field, in order to gain a deeper understanding of the interface creation under the supersonic wave conditions, to create reliable mathematical models of this phenomenon and to develop scale-up methodology for industrial devices.

SYNERGY FROM ENERGY: THE COMBINED TECHNIQUES

As one might easily guess, there are a number of attempts reported in the literature of using an alternative

Table 5. Process intensification effects of the alternative sources and forms of energy reviewed in this paper.

Energy source	Form of application	Intensified element	Reported magnitude of possible improvement as compared to conventional technology (approx.)
High-gravity field	Spinning disc reactor	Heat transfer from liquid film	15 times
		Mass transfer in liquid film	10 times
		Reaction time	1000 times
		Equipment size	100 times
		Impurities level	>90%
	Rotating packed bed	Liquid-side mass transfer	200 times
		Gas-side mass transfer	9 times
Electric field—static	Extraction systems	Heat transfer from droplets	3 times
		Mass transfer	10 times
		Interfacial area (by emulsification)	500 times
	Boiling liquids, evaporators	Heat transfer	10 times
Electric field—dynamic (gliding arc)	Gaseous non-catalytic reactions	Energy consumption	No comparative data available
		Equipment size	No comparative data available
Electromagnetic radiation—microwaves	Liquid-phase (catalytic) reactions	Reaction time	1250 times
		Product yield	10% (average)
	Gas-phase catalytic reactions	Conversion, product yield	Several times (depending on temperature)
	Distillation	Distillation time	20 times
Electromagnetic radiation—light	Photocatalytic reactions	Product yield/selectivity	Several times, in some cases 100% selectivity can be achieved, not achievable by conventional methods
		Energy (in sunlight driven processes)	No comparative data available
Acoustic field	Ultrasound irradiation	Reaction time	25 times
		Product yield	In some cases 100% yield of the product which could not be synthesized at all via conventional method
		Gas–liquid mass transfer	5 times
		Liquid–solid mass transfer	20 times
	Low-frequency acoustics	Gas–solid mass transfer	3 times
		Gas–liquid mass transfer	2 times
Flow	Hydrodynamic cavitation	Reaction time and product yield	Similar as with ultrasound, however 10 times higher cavitation yield
	Supersonic flow	Gas–liquid mass transfer coefficient	10 times
		Fluid-bed reactor capacity	2.25 times

source of energy in combination with another source. Such a combination is expected to have a synergistic effect on process efficiency, or at least increase it by combining the individual effects.

Already in 1967 Denis patented an electric discharge apparatus for chemically reacting flowing gases, in which low-temperature, low-pressure reactions could be conducted in a non-catalytic way, by applying electrical discharges to the gas stream accelerated to supersonic velocity. Methane decomposition to acetylene and hydrogen, ethylene and tetramethyl ethylene oxidations with ozone, production of hydrogen chloride and formaldehyde were mentioned as exemplary processes. A combination of high-gravity field and photochemical processing was investigated by a number of authors. The SDR was studied for UV-initiated polymerization of butyl acrylate (Dalglish *et al.*, 1999; Boodoo *et al.*, 2001), as well as for TiO_2-based photocatalytic oxidation processes (Yatmaz *et al.*, 2001; Dionysiou *et al.*, 2002). Microwave-assisted photochemical processes were also investigated. Kataoka *et al.* (2001) observed an almost two-fold increase of conversion when a photocatalytic reactor for ethylene oxidation has been subjected to microwave irradiation. A good detailed review on microwave photochemistry was published by Klán and Církva (2002). Also sonophotocatalytic reactors were investigated, basically in application to wastewater purification. The role of ultrasound in such reactors is not only to activate the reactions by implosions of microcavities, but also to clean and sweep the catalyst surface (fouling prevention) and to facilitate the reactants transport to it. Recent paper by Gogate and Pandit (2004b) brings a good overview of the research work done in this area. Last but not least, effects of simultaneous irradiation by microwaves and ultrasound ('microwave sonochemistry') were also studied (Maeda and Amemiya, 1995; Chemat *et al.*, 1996). The application of microwave sonochemistry to pyrolysis of urea resulted in 25% increase of the product yield (cyanuric acid) as compared to both the conventional method and to the microwave-only method. In case of the esterification of propanol with acetic acid the corresponding improvements were 24% and 9%, respectively (Chemat *et al.*, 1996).

CONCLUSIONS

The present review leaves little doubt about the potency of some alternative sources and forms of energy as tools for intensification of chemical and biochemical processes. Depending on the type of energy applied, different elements in the process can be influenced and the resulting effects differ in magnitude, as it is shown in Table 5.

Some of the alternative sources and forms of energy, such as high-gravity fields, have already been applied on the industrial scale. For many others, however, the chemical engineering community has not been able until now to develop technically and economically feasible solutions. One of the reasons is definitely a very modest involvement of chemical engineering in those research areas, so far. As an example, I estimate that only less than 5% of all research papers published on microwave-assisted reactions originate from the chemical engineering world. The basic *engineering* understanding of the mechanisms behind the alternative energy-based processes and of the relations between various parameters influencing those processes is still insufficient. In order to apply more alternative sources and forms of energy for intensification of chemical or biochemical manufacturing, a more intensive research effort of the chemical engineering community in those areas is needed. Close research collaboration with other disciplines, chemistry, material science and applied physics in particular, will be here of crucial importance.

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