REVIEW

Microwave Synthesis, Extraction, Improvement and Degradation in Oil Chemistry

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Abstract: This review article summarizes research directed toward microwave heating in the oil chemistry. Topics to be discussed include microwave synthesis of surfactants, extraction methods, modification of crude oil properties, and degradation of surfactants. The specific effects of microwave heating, which cannot be obtained by conventional heating in particular, are explained.

Key words: microwave, synthesis, extraction, improvement, degradation

1 Introduction

Microwave radiation represents electromagnetic radiation spanning the frequency range of 30 GHz to 300 MHz, i.e., it spans the range of wavelengths from 1 m to 1 cm (Fig. 1). Such wavelengths impart molecular behaviors different from those of molecules that are subjected to shorter wavelength radiation (*e.g.* UV, visible and infrared). Phenomena such as vibrations of electrons (electron polarization) and molecules (ion polarization) are commonplace on molecules exposed to various short-wavelength electromagnetic radiation ranges. In contrast, radio waves with wavelengths longer than infrared give rise to molecular alignment (i.e. alignment polarization).

Two rather familiar devices that make extensive use of this low-energy radiation are the microwave cooking oven and the cellular phone. Early industrial examples of microwaves in manufacturing (1949 and onward) include the thermal molding of wood and plastics, as well as the drying of medicinal products, fibers, teas, and cigarettes. In recent years, microwaves have also been used in cancer treat-

ments (hyperthermia), in drying and sterilizing foodstuffs, and in vulcanizing rubber, among others. In the chemical and material sciences, fundamental microwave research in the mid-1970s focused on the microwave heating of inorganic materials, with some active research in the early 1980s being directed at the microwave sintering of ceramics¹⁾ in which the principal feature was the formation of compact crystal grains in short times at relatively low temperatures. In the organic field, microwave irradiation to drive organic syntheses was not explored until the mid-1980s, i.e., not until the first two reports in 1986 by Gedye *et al.*²⁾ and Giguere and coworkers³⁾ on microwave-enhanced organic syntheses. Since then, many organic chemists have discovered the benefits of microwave irradiation to drive chemical reactions, which has, as a consequence, driven industrial growth in the manufacture of microwave ovens specifically designed for research laboratories. In this regard, the number of reports on the use of microwaves as an energy source to assist chemical reactions has experienced an astronomical growth since the earlier

	X-ray	UV	Visible	IR	Microwave	Radio wave
Frequency (Hz)	10 ²⁰		10 ¹⁵		10 ¹⁰	10 ⁵
Wavelength (m)		10 ⁻¹⁰		10 ⁻⁵		1

Fig. 1 Classification of electromagnetic waves.

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Fig. 2 Number of papers by using the keywords 'microwave' and 'organic synthesis'.

decades (Fig. 2)⁴⁾.

Research into microwave heating for chemical reactions has garnered significant attention in the past twenty years; particularly, awareness of so-called "microwave effects," which cannot occur through conventional heating, has received great interest. Researchers have applied microwave irradiation specifically toward synthetic organic reactions⁵⁾, where it has been generally found that the synthesis of organic materials is remarkably accelerated by microwave heating compared with conventional heating methods. Additionally, the synthesis of nanoparticles has also been explored with respect to chemical reactions using microwave heating⁶⁾, where a uniform nanoparticle size can be quickly formed by the microwave method.

The mechanisms of microwave and conventional heating are different—the following describes the interactions between microwaves and substances being irradiated, as well as their features⁷⁾. On conventional heating (e.g. oil bath, electrical heater, etc.), thermal energy from a heat source is transferred to the sample solution by conduction, convection and radiation. In contrast, microwave heating can directly heat the molecules comprising the substances themselves through energy absorption. As noted above, the heating mechanism for microwave irradiation is drastically different from that of conventional heating.

An important process of energy conversion involves converting microwave energy into thermal energy⁸⁾. Generally speaking, there exist three types of heating by microwaves: (i) dielectric heating; (ii) conduction loss heating, and; (iii) magnetic loss heating. For instance, induction heating by the microwaves' magnetic field is expected to occur in catalyzed reactions involving solids, an example being the rapid induction heating of magnetite (Fe_3O_4) but not hematite (Fe_2O_3) as the latter is not a magnetic material⁹⁾.

The thermal energy P produced per unit volume originating from microwave radiation is given by Equation 1:

$$P = \frac{1}{2} \sigma |E|^2 + \pi f \epsilon_0 \epsilon'' |E|^2 + \pi f \mu_0 \mu'' |H|^2 \quad (1)$$

where $|E|$ and $|H|$ denote the strength of the electric field

and magnetic field of the microwaves, respectively; σ is the electrical conductivity; f is the frequency of the microwaves; ϵ_0 is the permittivity in vacuum; ϵ'' is the dielectric loss factor; μ_0 is the magnetic permeability in vacuum; and μ'' is the magnetic loss factor. The first term in Eq. 1 is representative of conduction loss heating; the second term denotes dielectric loss heating, whereas magnetic loss heating is given by the third term. Microwave heating of solutions is ruled mostly by dielectric loss heating, whereas conduction loss heating involves mostly solid materials. Generation of heat by magnetic loss heating is expected only in magnetic (solid) materials. A catalyzed reaction occurring on a solid catalyst is expected to show characteristic differences with the solution bulk because the reactant substrates in the liquid are adsorbed on the solid surface. Temperature rise in systems involving solely gaseous molecules is negligible because the molecular density is small.

Conduction loss heating: The hydroxide ion is a typical ionic species with both ionic and dipolar characteristics. For solutions containing large amounts of ionic salts, the conductive loss effect can become larger than dipolar relaxation. For solids, conduction losses tend to be slight at ambient temperature but change substantially with an elevation in temperature. As for the typical example, the dielectric loss of alumina (Al_2O_3) is negligibly small ($\sim 10^{-3}$) at room temperature. However, it can be melted by microwave in a short time (minutes). This effect arises from a strong increase in conduction losses associated with the thermal activation of electrons, which migrate from the oxygen $2p$ valence band to the $3s3p$ conduction band of alumina. Moreover, conduction losses in solids are usually enhanced by defects in the materials, which sharply reduce the energy gap between the valence and conduction bands. To the extent that conduction losses are high for carbon black powder, it is often used as added loss impurities or additives to induce losses within the solids for which dielectric losses are too small.

Dielectric loss heating: A mechanism by which a non-conductive material can be heated by the microwaves' electric field involves molecular rotation of the molecules' electric dipole moment, which aligns itself with the field. As the field alternates, the molecules reverse direction and accelerate the motion of individual molecules or atoms, thereby generating heat through friction of the molecules rotating against each other. Dielectric heating can therefore be applied to the heating of solutions. By contrast, heating of electro-conductive solids, such as metals, implicate ohmic losses in the material by virtue of the current flow induced by the oscillating electric field.

Magnetic loss heating: For metal oxides such as ferrites and other magnetic materials, magnetic losses occur in the microwave region. These losses are different from hysteresis or eddy current losses because they are induced by the presence of a domain wall as well as electron-spin reso-

nance. Such materials are typically placed at positions of magnetic field maxima for the optimal absorption of microwave energy. Transition metal oxides such as those of iron, nickel, and cobalt possess high magnetic losses and can thus be used as additives to induce losses within the solids having low dielectric loss factor.

Considering water-in-oil (W/O) emulsion samples, for instance, dielectric loss of oil as the continuous phase is too low to be heated effectively by microwave irradiation. On the other hand, dispersed water drops can be selectively heated by microwave irradiation; this selective heating of water is a phenomenon specific to microwave heating. The major frequency of the microwave heating is 2.45 GHz (wavelength of *ca.* 12.24 cm), it is far larger than molecular size. Therefore, emulsion size is an important factor that determines the heating efficiency by microwave. On the other hand, the microwave-heating rate can be remarkably changed by the addition of inorganic ions as impurities¹⁰.

2 Microwave in oil chemistry

2.1 Synthesis of surfactants

Researchers have actively pursued the syntheses of biodegradable surfactants using microwave heating in recent years. For example, methods describing the synthesis of fatty acid esters of natural product origin such as cellulose have been reported^{11, 12}, in which obtained product yields and degree of substitution (DS) values were improved through the microwave synthesis method. Tomanová and co-workers reported the synthesis of a biodegradable polymeric surfactant via the transesterification of the methyl

esters in rapeseed oil and carboxymethyl cellulose (CMC)¹³. In the synthetic procedure, 4-toluenesulfonic acid, rapeseed oil, CMC and catalytic potassium carbonate were added to *N,N*-dimethylformamide or water solvent; the resulting solution was heated by microwave irradiation. The chemical yield with conventional methods was 81% (DS = 0.08) at a reaction time of 4 h. On the other hand, the microwave method gave the same yields (DS = 0.06), but did so in a reaction time of only several minutes. The synthesized surfactant had a surface-active function similar to that of a commercial surfactant (Tween 20). Moreover, since the mass number of CMC after microwave irradiation decreased, the depolymerization of the cellulose structures of CMC was improved by the microwave irradiation. Change of depolymerization has also been reported by the other researches, which has discussed the dependences with solvents. A polymeric surfactant comprised of polyoxyethylene (23) lauryl ether and sucrose was synthesized by a one-pot procedure *via* microwave heating under solvent-free conditions¹⁴. Polyoxyethylene (23) lauryl ether, sucrose and potassium persulfate (KPS) as catalyst were mixed in the absence of solvent, followed by microwave irradiation for 5 min. A proposed mechanism involves the formation of an O[•] radical from the hydroxyl moiety on the pyranose ring of sucrose by microwave irradiation, followed by its reaction with a lauryl ether radical (Reaction 1). Although a reaction time of 10 h was required in the conventional heating method, this could be shortened to 5 min by microwave.

A novel microwave preparation method of nonionic surfactant was proposed¹⁵. A monocationary surfactant was synthesized by the two-step reaction of peracetylated sugar and ω -undecanol (Reaction 2).

Reaction 1

The remarkable shortening of reaction time was indicated as a feature of the microwave in synthesis of the surfactant. Various discussions continue to appear in the literature about the elusive microwave-specific (non-caloric or non-thermal) effect(s) in organic synthesis¹⁶⁾ involving surfactants, besides the utilization of microwaves as a simple heat source. In many examples, specific microwave effects claimed in the past could easily be attributed to thermal (caloric) effects. However, some cases contrary to this are also observed. In comparison of microwave and conventional heating, the microwave-specific effect and thermal conduction model at the microscopic level were proposed in the synthesis of the monoglycerylcetyldimethylammonium chloride (MGCA) surfactant as a model reaction, in both homogeneous 2-propanol media and under solvent-free heterogeneous conditions¹⁷⁾. MGCA was synthesized under reflux conditions with 3-chloro-1,2-propanediol (CP) and *N,N*-dimethylhexadecylamine (DMHA) by microwave irradiation and by conventional heating at *ca.* 95°C (Table 1).

Differences in the time profiles of product yields in the synthesis of MGCA under matched temperature conditions were negligible within experimental error. That is, the microwave thermal (caloric) effect(s) followed closely conventional heating to yield nearly 31–32% products after *ca.* 30 min. Next, MGCA surfactant was synthesized in a solvent-free heterogeneous system using CP and DMHA substrates without 2-propanol solvent to avoid its influence on Reaction 3. CP and DMHA were physically mixed by magnetic agitation and appeared as a homogeneous phase when viewed macroscopically. The corresponding yields of MGCA were 62% (microwave heating) and 47% (oil-bath heating) after a 30 min heating period without solvent. Microwave heating can, in principle, induce localized hot spots that can lead to localized reaction rate enhancements¹⁸⁾, and thus to uneven heating at the microscopic level as predicted from the dielectric factors. However, no microwave-specific effect(s) was apparent even though the reaction solution contained substrates of different dielectric characteristics when heated in homogeneous 2-propanol solvent by microwave dielectric heating. It is likely that the 2-propanol solvent masked whatever specific effect(s) the microwaves may have achieved.

Table 1 Chemical yields of MGCA using microwave heating and oil bath heating, occurring in 2-propanol media and in solvent-free conditions under reflux.

Reaction 3

Solvent	Heating source	MGCA yield/%
2-propanol	Microwave	32
	Oil bath	31
Solvent-free	Microwave	62
	Oil bath	47

The thermal conduction model portraying the initial stage of the synthesis of the MGCA surfactant at 130°C in the absence of 2-propanol is illustrated in Fig. 3a for microwave heating and in Fig. 3b for oil-bath heating. Macroscopically, the mixed CP and DMHA substrates formed a homogeneous solution upon vigorous magnetic stirring. At the microscopic level, however, it is relevant to emphasize that the solution is heterogeneous with CP domains (oil drop analogs) dispersed in the DMHA sea. The penetration depths of the microwaves into the CP domains are 12.5-fold greater than in DMHA (see Table 1), and the dielectric loss factors indicate that the CP aggregates are preferentially heated by the microwaves. Thus, the temperature of the CP domains is expected to be greater than the temperature of the DMHA sea. The heat radiated by the CP domains subsequently permeates to the DMHA as a result of thermal gradients established by microwave dielectric heating in accordance with the second law of thermodynamics. After microwave irradiation, the distribution of the CP domains in the sea of DMHA molecules tends to become smaller with rise in temperature.

Microwaves are electromagnetic waves having frequencies of 0.3–300 GHz. Therefore, there is no need to limit their use only to the most commonly used frequency of 2.45 GHz. However, some frequencies are protected as in-

Fig. 3 Proposed models showing the differences in heating the DMHA sea and CP molecular domains in the initial stages of the solvent-free synthesis of MGCA surfactant by: (a) microwave-generated heat (MW) and; (b) conventional heat (OB).

Reaction 4

dustrial, scientific and medical (ISM) bands, and have been reserved internationally for purposes other than communication¹⁹. The ISM bands are defined by the International Telecommunication Union-Radiocommunication (ITU-R) sector. The globally used frequencies are 2.45 ± 0.25 GHz, 5.80 ± 0.25 GHz, and 24.125 ± 1.25 GHz; other frequencies are established by each country. A frequency of 915 MHz is actively used in industry in some countries, including the United States. The microwave of 915 MHz frequency must be examined microwave leaks in periodic inspections after an application is submitted to the government. The microwave frequency used in Japan for defrosting food or drying wood is 915 MHz, although it is not identified as an ISM band in Japan. The synthesis of Gemini surfactants was reported using microwave 915 MHz in early research²⁰. Cationic Gemini-surfactant $\text{C}_{12}-\text{C}_2-\text{C}_{12}$ synthesis in a closed vessel was performed as a model reaction (Reaction 4).

The yields of $\text{C}_{12}-\text{C}_2-\text{C}_{12}$ surfactant obtained using a novel organic synthesis apparatus comprised of a 915 MHz microwave generator were investigated (Table 2). The yields of $\text{C}_{12}-\text{C}_2-\text{C}_{12}$ surfactants under 915 MHz microwave irradiation were about 1.7 times higher than those

under 2.45 GHz dielectric heating under identical conditions. In contrast, when using an oil bath, the yields of $\text{C}_{12}-\text{C}_2-\text{C}_{12}$ surfactant decreased threefold when compared to the microwave-mediated reaction. Synthetic yield increased clearly by using a frequency of 915 MHz. Additionally, the longer wavelength of 915 MHz is advantageous in that it permits the use of larger reactor sizes. The cross-sectional area of the waveguide for microwaves at the common 2.45 GHz frequency is 59.62 cm^2 ($10.92 \text{ cm} \times 5.46 \text{ cm}$). On the other hand, the cross-sectional area of the waveguide for 915 MHz microwaves is 306.65 cm^2 ($24.77 \text{ cm} \times 12.38 \text{ cm}$)²¹; correspondingly, a reactor twice as large can be introduced in the 915 MHz waveguide compared with the 2.45 GHz waveguide. Next, the $\text{C}_{12}-\text{C}_2-\text{C}_{12}$ surfactant was synthesized in a 500 mL closed reactor under 915 MHz irradiation (Table 2). A higher yield was obtained even though the reaction scale was 10 times higher than in the 2.45 GHz system. Note that when using a 500 mL solution in the 2.45 GHz system, it is necessary to use the multimode microwave system used in microwave cooking ovens and the efficiency declines.

Table 2 Chemical yields of Gemini-surfactant in 915 MHz and 2.45 GHz microwaves and oil bath heating using closed vessels.

Experimental condition	Yield / %
915 MHz (70 W; 50 mL; 140°C)	68
915 MHz (70 W; 500 mL; 140°C)	60
2.45 GHz (150 W; 50 mL; 140°C)	40
Oil bath (368 W; 50 mL; 140°C)	23

2.2 Microwave extraction in oil chemistry

Extraction of organic constituents from petroleum source rock has generally been performed with organic solvent by the Soxhlet method. However, the Soxhlet method has a problem of a VOC (volatile organic compounds) as environmental impact and cost of organic solvents. Recent research into this matter has examined the replacement of an organic solvent with supercritical CO₂ fluid. The supercritical CO₂ fluid method has been reported as having extraction capabilities for hydrocarbon yields five times that of the Soxhlet method²². Furthermore, longer-chain hydrocarbon compounds can be extracted efficiently²³. A further advantage to using supercritical CO₂ is that flow methods can be employed. On the other hand, supercritical CO₂ fluid systems are known to have a higher cost of equipment. Organic solvents used in the Soxhlet method can also be replaced with a nonionic surfactant solution, as extraction processes using a nonionic surfactant are considered as having a lower environmental impact and lower cost of operation. The extraction efficiencies of hydrocarbons—such as phenanthrene, anthracene, pyrene, and benzopyrene—from ground samples containing tar discharged from a gas manufacturing plant were improved by Soxhlet extraction with a nonionic surfactant²⁴.

Schmidt and co-workers used aqueous nonionic surfactant solutions as extraction solvents for microwave-assisted solubilization of aliphatic and aromatic hydrocarbons from petroleum source rock. The relationship between amount of extracted hydrocarbon to the input value and irradiation time of microwave was examined. The extracted amounts of aromatic compound were not found to have a correlation with microwave output value, but rather it was shown that the amount is greatly dependent on temperature²⁵. In contrast, the extraction rate of aliphatic compounds fell with an increase in a microwave input power. Furthermore, the optimal extraction temperature was 90–105°C in aliphatic compounds, with extraction efficiencies falling above 120°C. Extraction temperature conditions suitable for relevant hydrocarbon compounds have been reported²⁶. A key feature of the microwave method described above is that extraction of aliphatic compounds is remarkably more effective than by conventional methods.

2.3 Property modifications of crude oil using microwave heating

The de-emulsification of W/O emulsions, removal of carboxylic acid, and desulfurization of oils have been considered as processes suited to microwave heating. In general, aromatic and aliphatic hydrocarbons can form W/O and O/W emulsions with water in crude oil, making the separation of water as an impurity from crude oil more difficult. It is necessary to de-emulsify the crude oil to make aqueous impurities in the oil phase separate. Compared with conventional heating methods, de-emulsification is known to be promoted by microwave irradiation; it is reasoned that the viscosity of emulsion solutions fall under microwave irradiation, improving de-emulsification efficiencies²⁷. Such a phenomenon cannot be acquired by heat tracing, which uses heat conduction. In addition, Nielsen and co-workers examined the frequency effect (range of 0.3–100 GHz) in de-emulsification²⁸. In order to obtain high de-emulsification efficiencies, a frequency in the range of 3.1–60 GHz was required, with 20 GHz found to be the most suitable frequency. The optimal frequency was observed to change with increases in salt concentrations to 0.6–1.8 GHz. Fortuny and co-workers examined influence of the water impurity content, salinity, and pH in efficiency of de-emulsion²⁹. Changes in the size of the W/O emulsion (3.5–100.1 µm) and the influence of heat by microwave was investigated. An increase in emulsion size made the dewatering ratio increase. The de-emulsification process was prevented by higher pH and salt concentrations; these conditions contribute to an increase in solution conductivity. Therefore, since the penetration depth of microwave fell, heating efficiency decreased¹⁰.

The naphthenic acid contained in crude oil shows surfactant-like characteristics. The naphthenic acid stabilizes dispersed water in crude oil as W/O emulsion. Since microwave absorption of crude oil is low, the heating of crude oil does not occur readily. Therefore, when crude oil samples containing W/O emulsions are irradiated with microwave, the aqueous phase will be heated selectively. The temperature distribution between the oil phase and water phase results in a change of the naphthenic acid tertiary structure, where the hydrophilic group and hydrophobic group of naphthenic acid are twisted according to the temperature distribution (Fig. 4)³⁰.

Property modification processes exist in which solid catalysts are employed in the refinery process of heavy oil. Research into the selective heating of heterogeneous catalysts by microwave irradiation in crude oil has experienced recent growth. Since the heavy oil and catalyst are heated simultaneously under conventional heating methods, application of microwave heating has been actively explored to carry out differential heating of only the catalyst in order to reduce energy consumption. A temperature gradient generated between the heavy oil and catalyst surface is a

Fig. 4 Proposed mechanism of de-emulsification of W/O emulsion with naphthenic acid under microwave radiation.

key feature of the microwave method. Therefore, disconnection of the substance from the catalyst surface is promoted and catalyst activity is maintained³¹. Furthermore, since differential heating of the reaction field is carried out, side reactions can be inhibited. For example, in the desulfurization of thiophene using $\text{Co/Mo/Al}_2\text{O}_3$ catalyst, using identical temperature conditions (1,000 K) with the conventional and microwave heating method, reaction efficiency increased two-fold with microwave heating³². Roussy and co-workers have carried out the microwave-mediated conversion reaction of methane to ethane or ethylene using $(\text{SmLiO}_2)_{0.8}(\text{CaOMgO})_{0.2}$ catalyst³³. The reaction rates and product selectivities were different between conventional and microwave methods.

2.4 Surfactant degradation by microwave methods

Global production of surfactants totals around 7.2 million tons per year, and comprises a substantial portion of total synthesized chemical products. Notwithstanding their industrial applications, surfactants are also chemical substances that exert an influence on the environment and vital ecosystems. Therefore, research directed toward surfactant degradation techniques have been actively pursued. For example, the degradation of anionic surfactants³⁴ and nonionic surfactants³⁵ using anaerobic bacteria as a biochemical processing method has been reported; however, a very long processing time is needed. Methods for easy and prompt decomposition of surfactants are a necessity for environmental protection.

The decomposition of organic compounds in water has

been examined with pure activated carbon (AC) under microwave irradiation. Plasma generated on the activated carbon by microwave irradiation promoted the decomposition of phenol, present as an aqueous organic pollutant³⁶. Bo and co-workers have reported the decomposition of *p*-nitrophenol in water by the formation of plasma³⁷. Sodium dodecyl benzene sulfate (SDBS) surfactant is known to decompose in the presence of $\text{Fe}_3\text{O}_4/\text{AC}$ by microwave irradiation³⁸. 73% SDBS (100 mg L^{-1}) in water was decomposed by microwave irradiation for 90 sec (Fig. 5). Since partial heating (hot-spots) arose near Fe_3O_4 on the activated carbon surface, the decomposition of SDBS was promoted by microwave irradiation (Fig. 6).

3 Concluding remarks

Thousands of examples of chemical reactions using microwave techniques have been reported in the past decade. The utility of microwave irradiation is based on the remarkable promotion of chemical reaction rates. Furthermore, research efforts into microwave-specific effects on chemical reactions are also being actively pursued. However, development of microwave applications in the oil chemistry field has not been as active. The microwave is easily applicable to the synthesis, purification, extraction and degradation of surfactants, oil and fats. Furthermore, in two-ingredient mixture systems, such as oil and cold water, the differential heating of emulsions by microwave can gener-

Fig. 5 UV-Vis spectra of SDBS solutions (diluted twice) under different conditions (experimental conditions: SDBS concentration of 100 mg L^{-1} , activated carbon particle dose of 1.20 g L^{-1} , solution acidity of pH = 6.0 and total volume of 25 mL). a: Original solution; b: microwave alone (90 sec); c: activated carbon (no microwave irradiation); d: activated carbon and microwave (90 sec).

Fig. 6 Illustration of degradation of SDBS on the surface of modified ACs.

ate favorable conditions that cannot be achieved using existing conventional heating methods. In the future, microwave chemistry will further spread and become established in the oil chemistry field as a viable technique in numerous industrial applications.

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