Chemical Reactor – Polymerizer

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Abstract- This paper describes the structure of a chemical reactor-polymerizer with magnetically stimulated polymerization process. The structure has no analogue in the practice of chemical industry but has not yet been the subject of practical implementation. Given the large-scale environmental issues and energy deficit, however, such a reactor can find application in a number of polymerization processes carried out via a radical mechanism. This is substantiated by the fact that based on experimental data, the reactor's structure has been approved and patented. The data have been obtained after prolonged research and show that it will be reasonably expedient to construct a reactor with the structure described in this paper.

Keywords- Industrial Magnetochemistry, Chemical Reactor, Polymerizer

I. INTRODUCTION

No case is yet known in which magnetic energy has been practically used as a kinetic factor in chemotechnological processes. In this respect, the heat energy has a remarkable priority. This fact is explained by the objectively existing thermodynamic limit which renders impracticable the possibilities for effective magnetic impact on chemical processes. For example, while the minimum activation energy that is required in chemical reactions normally exceeds 10 Kcal/mol, a very strong magnetic field, with a value of magnetic induction (B) of about 10 Tesla {B[T(10)], may induce an equivalent activation energy of only about 0.03 Kcal/mol on paramagnetic molecules. As is apparent from the Arrhenius rate constant ($k = Ae-\Delta E/RT$) equation, however, k does not depend only on kinetic but also on entropic factors. Respectively, substantial magnetic effects on the A factor are possible if states that possess different properties (i.e. triplet states and singlet states) are involved in a rate-determining step whose rate constant is given by k [1].

There is a large number of mainly organic chemical reactions occurring through a radical mechanism whose specificity makes it possible to overcome the mentioned thermodynamic limit. In those reactions, the Wigner spin conservation rule is not observed [1]. This leads to extension of the transition state of the reaction and allows for an energy-free (entropic) control over the ST/TS electronic transitions (intersystem crossing) of valence electrons using an externally applied magnetic field. The analysis of the results described in the quoted reference sources [1-8] and [9,10], in particular, categorically leads to the conclusion that the polymerization of vinyl, acrylic and methacrylic monomers in a magnetic field (and not only), as a chemical mechanism, is implemented in terms of two groups of differing in type but functionally related physical processes: thermodynamic and quantum mechanical.

Thermodynamic processes are temperature dependent. They lie at the basis of the classical collision theory [11], mainly through the concepts of the activation energy (Ea), the frequency of successful collisions and the rate constant (frequency factor A, rate constant k). Attention is paid to successful collisions occurring between activated molecules when in a suitable steric state. These are the main preconditions for the realization of the quantum mechanical processes.

The quantum mechanical processes are magnetically dependent. They are associated with the collision theory through the concepts of the so-called activated complex [11], in the physical nature of which interactions between the valence electrons of chemical reactants occur. It must be pointed out that the said classical concepts are currently considerably expanded and supplemented, thanks to the results obtained from the work in an externally applied impulse magnetic field (IMF) [9,10].

The possibility to use an externally applied IMF in the chemotechnological processes is especially productive in bulk, solution and dispersion radical polymerization processes. For example: Donor/Acceptor Radical Copolymerization (DARC) [3,4] in which the yield can increase more than seven times {(depending on the Q-e parameters of comonomers [12]}, or in Atom Transfer Radical Polymerization (ATRP) [5,6] in which the yield can increase over two times. In addition to the increase of the yield, the use of IMF with appropriately selected parameters reduces the working temperature, lowers the quantity of used initiators (catalysts) and shortens the duration of processes. It may be expected that, when using IMF, it would be possible to exercise technological control on other radical processes occurring during prolonged transition states of complex formation, for example: the synthesis and vulcanization of rubber, and even some industrial microbiological processes.

II. Organization of the Experimental Work

A. Laboratory Equipment

A permanent magnetic field (PMF) and an impulse magnetic field (IMF) - with adjustable value of magnetic induction (B) and ripple coefficient (P) at a fixed frequency (f) of the unipolar non-sinusoidal impulses - are obtained through a solenoid inductor. In our experiments, we have used the following values of the characteristic parameters of magnetic fields:

1. Magnetic induction, B = 0.00; 0.05; 0.10; 0.15; 0.20 and 0.25 T.

2. Ripple coefficient, P = 0 % for PMF; 32% and 133% for IMF.

3. Pulse frequency, f = 150 Hz for IMF.

The fixed value of the unipolar pulse component frequency (150 Hz) was selected to achieve a more convenient fitting, using readily accessible technical means, in a frequency range equal to the frequency of the industrial three-phase current (150 Hz).

The solenoid inductor is powered by a three-phase thyristor rectifier as a symmetrical Larionov bridge [13] which is distinctive in that the unfiltered rectified current contains non-sinusoidal, unipolar (with a positive polarity) pulses with a frequency of 150 Hz, equal to the frequency of the industrial three-phase electric current.

The value of the current running through the inductor is measured indirectly, taking into account the fall of the voltage on a precision current shunt connected to the electrical circuit of the inductor. Since the electrical resistance of the inductor coil is a constant value (0.40 Ω; 25°C), this makes it possible to determine the necessary current value by using the law of Ohm.

The need for an experimental flexibility has called for the construction of equipment with significant constructive resizing. In terms of structure, the inductor is made of an aluminium alloy (Si - 3%). It is designed as a cylindrical body (coil) with cavities in the walls allowing the flow of water to cool down the solenoid coil. Along the axis line of the housing, there is an opening (d = 110 mm) intended to host the cylindrical body, made of aluminium alloy, which performs the role of water (oil) bath. A heat sensor is mounted at the bottom of the bath to control the temperature of the coolant fluid. A separator (carrier) is mounted in the bath during bulk, solution or dispersion homo- and copolymerizations. It is intended to maintain 12 glass ampoules for specimens, with a volume of 15 cm3 each, in the homogeneous zone of the magnetic field. There is a possibility to install a precision thermometer for temperature control in the ampoules. Where appropriate, instead of a separator, a three-neck flask with a volume of 100 cm3 can be mounted in the bath, equipped with monomer proportioner, stirrer, reflux condenser, control thermometer and inert gas purging system. This helps create conditions for work in a common volume, in a manner convenient for solution or dispersion polymerization, with a possibility to maintain the temperature with an accuracy of ± 0.5°C.

The magnetic induction value in the inductor's working space is regulated by adjusting the magnitude of electric current running through the coil. In advance (in the making of the inductor), by means of calibration measurement with the aid of magnetometer (Teslameter T-1; USSR), reference values of magnetic induction are determined in a tabular dependence: B= 0.05; 0.10; 0.15; 0.20; 0.25; 0.30, 0.35 T and their corresponding values of the current running through the inductor. Since the number of coils making up the solenoid of the inductor is a constant value (n = 270, s = 8 mm2), the reference values, as well as all random intermediate values of the magnetic induction, for each measured value of the voltage and the current running through the inductor, may be determined by calculation.

The magnitude of the current impulse component is regulated through additional inclusion in the inductor circuit of different-sized inductances (L) and capacities (C), which makes it possible to achieve a different, but strictly determined in value, ripple coefficient (P). This coefficient is defined as the percentage of the ratio between the effective value of the current with an impulse component (Iimp.EF.) and that of an equivalent constant current (Iconst.) running through the inductor, respectively: P (%) = (Iimp.ef./Iconst.).102. At certain values of L {L[H(3.00)]} and C {C[μF(47,000)]}, a permanent magnetic field with P 0.00% is practically obtained. At L 0.00 H and C 0.00 μF, P 133% is obtained. At L 3.00 H and C 0.00 μF, P 32% is obtained. In this case, the impulse magnetic field has the highest efficiency for the polymerization process.

Following a repeated experimental verification, the described laboratory device was used as the prototype of the patented, structurally developed conceptual design of the "Chemical Reactor - Polymerizer" [14]. It is characterized mainly with that about 70% of the total magnetic flux is obtained from permanent magnets while the remaining about 30% is obtained from pulsed electromagnets powered by an impulse generator.

B. Basic Experiments

To carry out the basic experiments, the widely available vinyl, acrylic and methacrylic monomers were used, by recording the impact of Q-e parameters of comonomers [12]. Polymerizations were carried out in bulk, in solution and in dispersion without magnetic field (WMF), in PMF with P 0.00%, in IMF with P 133% and in IMF with P 32%.

1) Donor/Acceptor Radical Copolymerization (DARC):

The method is used to perform copolymerization between vinyl neodecanoate {VND[Shall(Veo-Va)]} and maleic anhydride (MA) in a 1:1 ratio, respectively: 6.62 g MA – 6.8 x 10-2 mol; e = 2.25 и 13.378 g VND – 6.8 x 10-2 mol; e = -0.53. To obtain a 50% w/v solution in a flask (100 cm3), 17.5 cm3 dichlorethane are added. The flask is purged with nitrogen for 25 min., then 0.08 g (3.3 x 10-4 mol) benzoyl peroxide are added and heated to 80°C, and then 10 samples of 3 cm3 are extracted every 2 min. Copolymer is precipitated with ethyl alcohol and dried to a constant weight at 50°C in vacuum [15].

The efficiency of DARC in conditions of WMF, PMF or IMF at B = 0.15 T and different P values is represented in

Table 1 by comparing the conversion (qmas%), the specific viscosity (ηsp; 1% solution in dioxane) and the initial velocity of copolymerization (Vpmol/l.s).

Parameter	WMF	PMF; P = 0%	IMF; P = 32%	IMF; P = 133%
qmas%	35.84	47.45	70	59.03
ηsp	0.6068	0.6427	0.6615	0.5128
Vp, mol/l,s	1.9x10-3 mol/l.s	3.7x10-3 mol/l.s	8.7x10-3 mol/l.s	5.5x10-3 mol/l.s

The data in the table show that the efficiency of DARC is the highest when working in IMF, at B = 0.15 T and a ripple value P = 32%.

2) Atom Transfer Radical Polymerization (ATRP):

The method is used to perform homopolymerization of 2-hydroxyethyl methacrylate (2-HEMA) in a solution of methyl alcohol (50 % w/v), at 20°C in WMF, PMF and IMF with B = 0.15 T and P 32% (without P 133%). The following components are placed in a 50 cm3 flask in a quantity for nine samples: ethyl-2-bromoisobutyrate - 0.153 cm3 (1.02 x 10-3 mol), 5 cm3 2-HEMA (4 x 10-2 mol), and 5 cm3 methanol. The solution is purged for 25 min. with nitrogen at room temperature. In nine tubes (10 cm3 each), 0.044 g (2.84 x 10-4 mol) of CuBr (cupro bromide) are placed. In accordance with a sampling schedule (5, 10, 20, 30, 45, 60, 90, 120 and 180 min.), 1.12 cm3 of the decarbonated solution are successively placed in them. The tubes are closed immediately because polymerization starts right after mixing the liquid with the solid phase. The polymer is precipitated in the tubes by adding 5 cm3 diethyl ether and is dried at 50°C in vacuum to a constant weight [16].

The efficiency of ATRP in conditions of WMF, PMF or IMF at B = 0.15 T and the specified P values is represented in Table 2 by comparing the conversion (qmas%), specific viscosity (ηsp; 1% solution in methanol) and the initial velocity of polymerization (Vpmol/l.s).

Parameter	WMF	PMF; P = 0%	IMF; P = 32%
qmas%	53.01	57.95	73.06
ηsp	0.0510	0.0612	0.0918
Vp,mol/l.s	3.51x10-3 mol/l.s	4.95x10-3 mol/l.s	6.75x10-3 mol/l.s

The data in the table show that the efficiency of homopolymerization is the highest when working in IMF, at B = 0.15 T and a ripple value P = 32%.

III.   CHEMICAL REACTOR - POLYMERIZER

The present paper describes a patented project, in a conceptual stage, for the construction of a chemical reactor - polymerizer (CR-P), which is distinguished for providing an opportunity for magnetic stimulation of the polymerization process [14]. Because of its structure, CR-P is able to affect both the thermodynamic and quantum mechanical processes simultaneously, thus ensuring the effective conduct of the Donor/Acceptor Radical Copolymerization (DARC) and of the Atom Transfer Radical Polymerization (ATRP).

In a structural aspect, the described CR-P, other than by default, provides the opportunity for the conduct of bulk, solution and dispersion polymerization and copolymerization in the conditions of externally applied permanent or impulse magnetic field with adjustable magnetic induction at a value varying from 0.130 to 0.175 T and adjustable ripple coefficient from 27 to 35%. When conducting periodical technological processes, it is expedient that the height of the reactor does not exceed twice the diameter. It is possible to use a ring-shaped tubular structure to perform semi-continuous technological processes in which at least one sector must be covered by magnetic inductor.

The technical structure of the CR-P consists of three main structural units: polymerization reactor body, cylindrical magnetic inductor and pulsed electric current generator.

A. Polymerization Reactor Body

Generally, it does not differ from the facilities that are practically applied for this purpose but is made of a diamagnetic material. The material to be used in the making of the reactor body needs to be diamagnetic in order to prevent the partial shunting of the resultant magnetic flux through the reactor housing. Such requirement is met by materials such as glass, porcelain, non-ferrous metals and many varieties of stainless steel which are generally used in the making of chemical devices.

B. Cylindrical Magnetic Inductor

It comprises several symmetrically mounted permanent magnets and evenly spaced between them pulsed electromagnets. It is designed with an option to create, by means of permanent magnets, a basic permanent magnetic field with a magnetic induction of 0.100 to 0.125 T, making up 70% of the magnetic induction of the required total magnetic flux. The polymerization reactor body is mounted axially inside it. In a structural aspect, the magnetic inductor can be made in two versions: magnetic inductor with axial magnetic flux and magnetic inductor with radial magnetic flux, as shown on Figures 1 and 2.

The requirement for 70% of the total magnetic flux of the inductor to be generated by permanent magnets can be achieved by a large number of commonly used hard magnetic materials. Especially suitable are certain varieties of tungsten, chromium and cobalt steel as well as alnico alloys which may have a residual magnetic induction from 0.5 to 1.2 T and magnetic field intensity (coercive force) from 250 to 650 Oe [17,18]. In addition, these materials are technologically convenient - magnets with trapezoidal or cylindrical cross

section, appropriate for the particular case, are obtained by casting.

The requirement for 30% of the total magnetic flux of the inductor to be generated by pulsed electric current is achieved by means of pulsed electromagnets constructed as winding coils of copper wire wound on the insulating bodies installed symmetrically between the permanent magnets of the inductor. In the cavities of each insulating body are placed two cylindrical ferromagnetic bodies made of soft magnetic material (low-carbon steel), one of which is firmly fixed on the one magnetic pole and the other one is longitudinally flexibly connected on the other magnetic pole. These bodies simultaneously fulfil the role of a ferromagnetic nucleus for the relevant pulsed electromagnet and of an adjustable magnetic shunt. With its aid, by moving the flexible body in relation to the fixed one, the air gap can be changed in a controlled manner and so can the magnitude of the total magnetic flux generated by the inductor.

1) Axial magnetic flux inductor (Fig. 1):

In a structural aspect, it consists of two flat rings (2,3) made of soft magnetic material (low-carbon steel), which function as salient magnetic poles and, due to their ring shape, generate magnetic flux with a maximum density in the interior cylindrical space. The internal diameter is such that it encloses the housing (1) of the CR-P externally. A certain number - 2, 3, 4 or more (depending on the volume of the CR-P) - permanent magnets (4) with trapezoidal or circular cross section, situated symmetrically to one another, at equal number of angular degrees, are installed structurally between the two planes of the rings. The same number of pulsed electromagnets (6 - coil, 7 - insulating body, 8,9 - magnetic shunt) are installed symmetrically between them. In order to satisfy the requirement for the maximum density of the total magnetic flux in the working volume of the CR-P and the structural condition for the ratio between the height and the volume of the housing to be approximately 1:2, two or more magnetic inductors may be connected in an assembly. This can be achieved by mounting them together on the housing of the CR-P so that unlike magnetic poles overlap in the point where they connect to each other.
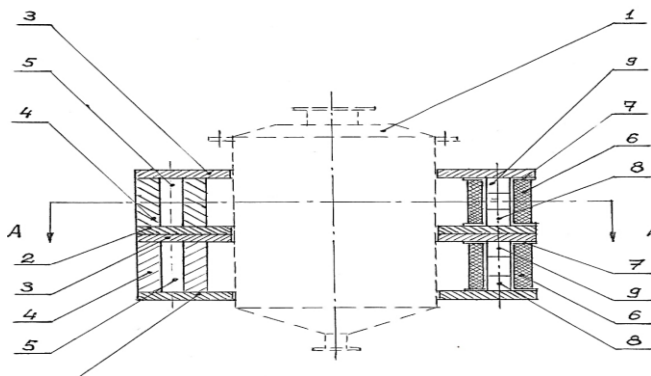

Figure 1.   Axial magnetic flux inductor

2) Radial magnetic flux inductor (Fig. 2):

In a structural aspect, it consists of outer cylindrical housing (2) made of soft magnetic material (low-carbon steel) which functionally fulfils the role of magnetic guide for the total magnetic flux of the inductor and joins the components in a common structure. Inside the housing, at 90 angular degrees, are mounted vertically one above the other, in four groups, two permanent magnets (4), and between them - one pulsed electromagnet (5 - coil, 6 - insulating body, 7,9 - shunt). To the inner end of each group of two permanent magnets and one pulsed electromagnet is mounted one arched pole piece (8) made of soft magnetic material (low-carbon steel), thus forming the four salient magnetic poles of the inductor, enclosing the outer housing (1) of the CR-P. Permanent magnets and pulsed electromagnets are installed between the cylindrical housing (2) and the pole pieces (8) in a manner that leads to the formation of diametrically opposed unlike magnetic poles. To avoid the formation of two perpendicularly intersecting magnetic fluxes, a hollow tubular ferromagnetic core (10) is mounted inside the CR-P, with an agitation mechanism mounted inside. The core is made from soft magnetic material (low-carbon steel) and closes the magnetic fluxes, thus contributing to the creation of a homogeneous magnetic field within the operating space. Where it is necessary to optimize the density of the magnetic flux in height, it is possible to join in an assembly two or more magnetic inductors.
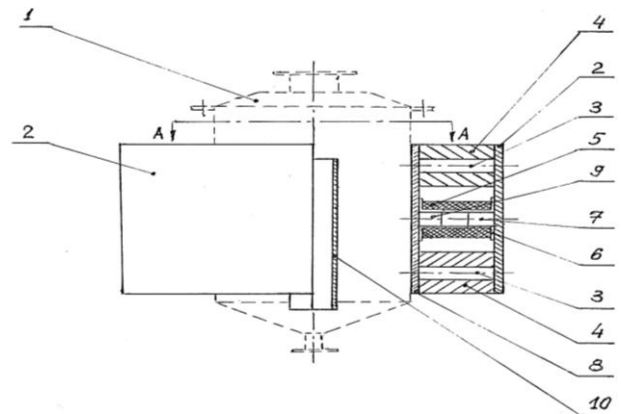

Figure 2.   . Radial magnetic flux inductor

C. Pulsed Electric Current Generator

The generator is designed to create pulsed electric current with a frequency of 150 H, adjustable in amplitude. The current that runs through the windings of the pulsed electromagnets, structurally joined with the magnetic inductor, creates an additional impulse magnetic field with a magnetic induction of 0.030 to 0.050 T, equal to 30% of the value of the magnetic induction of the total magnetic flux. In this way, it is possible for the total magnetic flux of the resultant magnetic field to have values of magnetic induction from 0.130 to 0.175 T, with a ripple coefficient varying between 27 and 35%.

The experience gained by the use of laboratory magnetic inductor shows that pulsed electromagnets can be powered by adjustable pulsed unipolar electric current with a frequency of 150 Hz, generated by three-phase thyristor rectifier according to the Larionov's or another circuit.

IV. CONCLUSION

No matter how attractive the idea of designing and building an industrially applicable CR-P might be, this is obviously a risky venture which can only be accomplished by a large investor. Certainly, there is a need for economic and technical means, resources for further laboratory research as well as for the construction of an experimental semi-factory and industrial equipment. Given that the conventional energy sources are still widely available and developing in an environment-friendly direction, the proposed CR-P might be perceived as yet another hypothetical idea. Nevertheless, the construction and technological study of an experimental semi-factory equipment may provide information that will not only help solve some of the environmental and energy issues but will also channel the theory and practice of the chemical industry into a new prospective field - Industrial Magnetochemistry.

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In the autumn of 1960, he was demobilized from the army with the qualification of Radio Location Station Operator. He is currently retired. He has been a General Director of the chemical enterprise "Himik" in the Bulgarian town of Razgrad for 22 years. He has published 25 scientific articles and holds 6 patents. Among his articles are "Spin Polarization Effect on the Hydroxyethyl Methacrylate Atom Transfer Radical Polymerization in Methyl Alcohol", Annuaire de L'Universite de Sofia "St. Kliment Ohridski", 2013 and "ATRP – Polarizing/Depolarizing Functional Mechanism" available online at ViXra.org, e-print archive, Chemistry, 1702(2), 2017