

# PROGRESS IN CHEMONUCLEAR AND RADIATION CHEMICAL PROCESS DEVELOPMENT

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In its broadest sense, the term "chemonuclear process" refers to any chemical production system which derives its motivating energy from a nuclear source. It should be recognized that nuclear energy can be transmitted either in the form of high energy radiation, or as thermal, electrical, or photolytic energy for inducing chemical reactions for production purposes. It thus becomes necessary to define further the type of chemonuclear system involved; for example, reference can be made to radio-, thermo-, electro-, and photo-chemonuclear systems, depending on which part of the continuous energy spectrum mainly controls the chemical process. Heretofore, the latter three levels of energy have been economically available from conventional fossil fuel and hydropower sources, and their utilization has become well established. It is mainly the relatively recent real prospects of the availability of massive sources of nuclear energy which provides the impetus for a thorough investigation of high energy radiation-induced chemistry and radio-chemonuclear processes, from both basic and applied points of view.

Massive sources of nuclear energy are becoming available either from nuclear fission reactors or from isotopic and electrically driven machine sources. High voltage machine radiation sources can also derive their prime energy from conventional power sources. The broad definition notwithstanding, the term chemonuclear process has been employed in a more limited sense to designate a process that makes direct use of a significant fraction of the energy of fission in a nuclear reactor for producing chemical products, while a radiation chemical process is accepted as one dealing with the indirect use of fission energy in the form of isotopic and machine sources. If in the nuclear reactor a significant fraction of the kinetic energy of the fission fragments is directly used to induce a chemical reaction, the term fission-chemonuclear has been applied and studies are thus progressing in fission-chemistry. Nuclear reactors that have already been developed and are in operation for thermal and power purposes use clad fuel elements and yield significant quantities of neutron and gamma radiation. When applied to chemical production, these may be referred to as  $n, \gamma$ -chemonuclear reactors. The variation in nomenclature is indicative of the relatively early stage of development of this field.

The careful work of the basic radiation chemists and physicists has provided some understanding of the primary processes in the interaction of high energy radiation with matter. Thus radiation is understood to cause a series of reactions resulting in ionization, excitation, and decomposition

of substances. In chemical synthesis processes we are interested in the breaking of chemical bonds and the reforming of new bonds to produce new chemical products. What are, therefore, the important factors in applying high energy radiation to the synthesis and production of industrial chemicals? To the engineer and industrialist the deciding factor depends on the economics. The economics of the system includes both the cost of producing the product and its quality or marketability. One can best illustrate the principal factors involved in the development of chemonuclear and radiation chemical processes by considering the following generalized relationship for evaluating the unit cost,  $C$ , of converting a chemical raw material into a unit of chemical product by means of a high energy radiation process:

$$C \approx \left( \frac{K}{GeMT} \right)^x.$$

$G$  is the  $G$  value or radiation energy yield for formation of the product and this indicates the requirement for an understanding of the radiation chemistry and kinetics of the system.  $e$  is the energy deposition efficiency or the fraction of energy available in the radiation source which is deposited in the chemical system and this indicates the importance of the design of the radiation source and reactor.  $M$  is the molecular weight of the product, which gives some indication of the type of product, and  $T$  is the production rate, which reflects both the size of the system and the extent of the marketability of the product. The constant  $K$  and the exponent  $x$ , which is  $> 0$  and usually  $< 1$ , are dependent on the type and size range of radiation source involved. The unit conversion cost is generally reduced as any one of the factors  $G$ ,  $e$ ,  $M$ , and  $T$  are maximized. Thus the radiation chemistry must be augmented by the nuclear reactor design and the requirements of product acceptability. It is insufficient to have a high  $G$  value and reactor efficiency when there is no need or ready market for a new product. Conversely, a product having a readily available market must have a sufficiently high  $G$  value and reactor efficiency to compete under the conditions of the existing market.

Generalizations can be made, based on quantity and cost of radiation, showing the relationship between type of chemical reaction and type of chemonuclear reactor. Non-chain reactions, which include all endothermic reactions and some exothermic reactions, have radiation  $G$  values ranging below 100, and usually below 10, while chain reactions, which are all exothermic, have  $G$  values above this range and which may reach into the millions. A range of reasonable and maximum values can also be assigned for the energy deposition efficiency. Fission-fragment reactors can be designed to operate with unclad, thin fuel elements giving energy deposition efficiencies reaching 50 per cent; clad element reactors, yielding essentially neutron and gamma radiation can have efficiencies in the range of 2-3 per cent of the total reactor power output; isotopic gamma radiators such as, for example, those employing  $^{60}\text{Co}$ , can be designed to allow utilization of 50 per cent of the total gamma radiation power available in the mass of isotope. With these efficiency values and assigning a molecular weight of 50 for an average industrial chemical product, the unit power level can be calculated as a function of  $G$  value, as is shown in *Figure 1*. For the low  $G$

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value non-chain reactions, it takes reactor power levels of the order of hundreds to thousands of kilowatts to produce one ton per day of chemical product. Industrial chemicals are usually produced at rates in the order of tens to hundreds of tons per day. Therefore, mainly fission-chemonuclear reactors can be considered to have reasonable power levels, in the range of tens to thousands of megawatts, for these low  $G$  value reactions.  $n, \gamma$ -chemonuclear reactors can be considered to have the right order of nuclear reactor

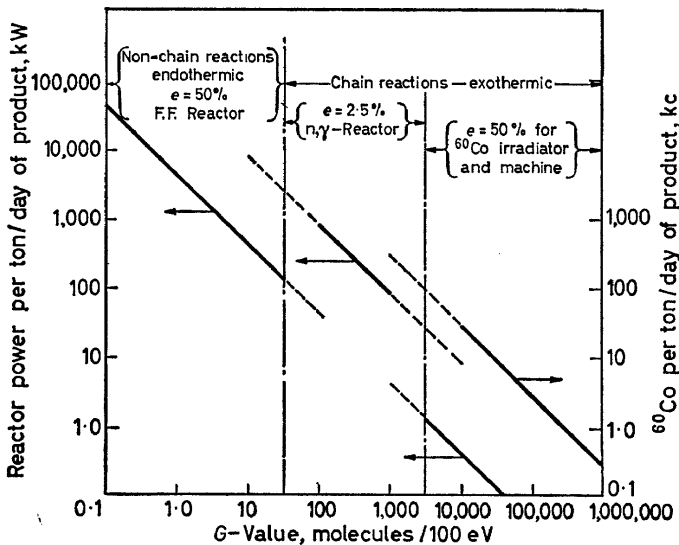


Figure 1. Chemonuclear reactors. Power requirement vs  $G$  value, for average product molecular weight of 50.

power levels for chain reactions having  $G$  values in the range of hundreds to thousands. Isotopic and machine sources are of value only for high  $G$  value chain reactions where power levels of the order of tenths of a magacurie to megacurie quantities of isotopic  $^{60}\text{Co}$  radiation are reasonable. For a direct cost comparison, it is generally recognized that isotopic and machine radiation costs today are about one dollar per kWh of radiation energy, and  $n, \gamma$ -reactor costs can be estimated at about 10 cents or one-tenth of a dollar per kWh, while fission-fragment radiation may be as low as tenths of a cent or one-thousandth of a dollar per kWh. Suffice it to say that fission-fragment energy promises the most abundant and lowest cost source of high energy radiation. Obviously, these generalizations must be modified by specific process and product evaluations.

By way of a survey, *Table 1* lists a number of endothermic chemical reactions which have been considered or proposed for chemonuclear synthesis<sup>1</sup>. Some of the reasons for choosing the reactions shown include the low value and high availability of the raw material and the high market demand of the product by the chemical industry. The radiation chemistry of some of these reactions has been studied to a greater extent than that of others. The figure of merit chosen to show how efficient a particular system is in producing the

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Table 1. Experimental  $G$  values and thermal efficiencies of endothermic reactions considered for chemonuclear processes<sup>1</sup>

Reaction	Product	Heat of reaction at 25°C, $\Delta H$ , (kcal/mole)	$G_{\max}$ (mol./100 eV)	$G_{\text{exp}}$ (mol./100 eV)	Thermal efficiency (per cent)	Type of radiation
$\text{H}_2\text{O}_{(l)} = \text{H}_{2(g)} + \frac{1}{2}\text{O}_{2(g)}$	Hydrogen	+68.3	33.8	1.7	5.0	F.F.
$\text{H}_2\text{O}_{(g)} = \text{H}_{2(g)} + \frac{1}{2}\text{O}_{2(g)}$	Hydrogen	+57.9	39.9	6.0 <sup>2</sup>	15.0	$\alpha$
$2\text{H}_2\text{O}_{(l)} = \text{H}_2\text{O}_{2(l)} + \text{H}_{2(g)}$	Hydrogen peroxide	+91.4	25.2	1.7	6.8	F.F.
$\frac{1}{2}\text{N}_{2(g)} + \text{O}_{2(g)} = \text{NO}_{2(g)}$	Nitrogen dioxide	+8.1	284	5 7.4	1.8 2.6	n, $\gamma$ F.F.
$\text{N}_{2(g)} + \frac{1}{2}\text{O}_{2(g)} = \text{N}_2\text{O}_{(g)}$	Nitrous oxide	+19.6	118	3.0	2.5	n, $\gamma$
$\text{CO}_{2(g)} = \text{CO}_{(g)} + \frac{1}{2}\text{O}_{2(g)}$ (with $\text{NO}_2$ inhibitor)	Carbon monoxide	+67.6	34.1	10.0	29.4	$\alpha$ and F.F.
$2\text{NH}_{3(l)} = \text{N}_2\text{H}_{4(l)} + \text{H}_{2(g)}$	Hydrazine	+48.0	48.1	0.13 1.9	0.3 4.0	$\gamma$ F.F.
$\frac{3}{2}\text{O}_{2(g)} = \text{O}_{3(g)}$	Ozone	+34.0	68.1	15	22.0	$\beta$
$2\text{CH}_3\text{OH}_{(e)} = (\text{CH}_2\text{OH})_{2(l)} + \text{H}_{2(g)}$	Ethylene glycol	+3.6	640	3	0.5	F.F.
$2\text{CH}_{4(g)} = \text{C}_2\text{H}_{4(g)} + 2\text{H}_{2(g)}$	Ethylene	+48.3	47.3	3	6.3	$\beta$
$2\text{CH}_{4(g)} = \text{C}_2\text{H}_2(g) + 3\text{H}_{2(g)}$	Acetylene	+90.0	25.6	0.5	2.0	$\beta$
$\frac{1}{3}\text{C}_6\text{H}_6(l) = \text{C}_2\text{H}_2(g)$	Acetylene	+49.0	47.0	0.42	0.9	$\beta$
$\text{CO}_{2(g)} + \text{H}_2\text{O}_{(l)} = \text{CH}_2\text{O}_{(l)} + \text{O}_{2(g)}$	Formaldehyde	+134.7	19.2	0.85	4.4	$\gamma$
$\text{CO}_{2(g)} + \text{H}_2\text{O}_{(l)} = \text{CH}_2\text{O}_{2(l)} + \frac{1}{2}\text{O}_{2(g)}$	Formic acid	+64.6	35.7	0.25	0.7	$\gamma$

Subscripts (l) and (g) refer to liquid and gaseous state.  
F.F. = fission fragment;  $\alpha$  = alpha; n = neutron;  $\beta$  = beta;  $\gamma$  = gamma.

desired product, is the thermal efficiency which is the approach of the experimental  $G$  value,  $G_{\text{exp}}$ . (molecules/100 eV) to the maximum value,  $G_{\max}$ , based on the minimum energy required for the reaction, as determined by the thermodynamic enthalpy or heat of the reaction,  $\Delta H$  in kcal/mole:

$$\text{Percentage thermal efficiency} = \frac{G_{\text{exp}} \cdot \Delta H}{23.07}$$

Most systems indicate efficiencies lower than 10 per cent, which from an applied point of view is relatively low. However, several items and interesting systems can be pointed out. First, there are relatively few experimental

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results available with high linear energy transfer (LET) heavy particle radiation, especially with fission fragment and alpha radiation, which as indicated earlier is needed for non-chain reactions. The radiation chemistry of liquid water for hydrogen and hydrogen peroxide generation has been extensively investigated, mainly with low LET gamma and beta radiation in non-flow systems. The best values in this system indicate efficiencies not exceeding 5 per cent. Some recent unconfirmed evidence<sup>2</sup> shows that the yield in the vapour phase may be higher, reaching efficiencies of 15 per cent or more. Relating this to some interestingly high  $G$  values for hydrogen-deuterium exchange in water vapour at higher temperatures<sup>3</sup>, further work on determining the effects of fission fragment radiation in high pressure water vapour and steam is indicated for evaluating a potential chemonuclear application.

The decomposition of carbon dioxide to form carbon monoxide in the presence of a nitrogen dioxide inhibitor is interesting because it shows an efficiency as high as 30 per cent. It is part of the function of the applied radiation chemist not only to understand the mechanism of the reaction but also to seek means for improving the efficiency of producing the desired product. The results obtained with the carbon dioxide-carbon monoxide system indicate that more work with scavengers and additives are needed in other systems.

The radiation yield for ozone with low LET radiation has indicated a relatively high efficiency of as much as 22 per cent. There is no radiation chemistry information available on the oxygen-ozone system with fission-fragment energy. An interesting result recently reported<sup>4</sup> suggests the possibility of inducing a chain reaction for formation of ozone during the oxidation of low concentrations of carbon monoxide in oxygen. Design and cost estimates indicate that it may be possible to produce ozone from oxygen economically at  $G$  values  $\geq 6$ .

The results of experimental work on the production of hydrazine<sup>5</sup> from fission-fragment irradiation of ammonia have been encouraging with respect to concentrations attainable. Costly experimental difficulties which were encountered, as well as the relatively small market for hydrazine, indicated that a continued pilot plant demonstrated of the feasibility of this system is not warranted at present. However, further radiation chemistry experience to provide an understanding of the ammonia-hydrazine system seems of definite interest.

In addition to those shown in *Table 1* there are probably other reactions which can be considered. Studies of new reaction systems are needed; for example, carbon-nitrogen, sulphur-nitrogen, and inorganic reduction reactions are possibilities.

A solution to the problem of improving the thermal efficiency in many of the radiation systems investigated to date may lie in recovering the unutilized degraded radiation energy for promoting thermal and low energy electron-induced chemical reactions in dual-purpose systems. To accomplish this will require investigation of radiation chemistry at higher temperatures, which is discussed later.

Turning to exothermic reactions, *Table 2* summarizes some of the systems of interest. Here thermal efficiency has no meaning unless it can be related to an activation energy<sup>1</sup>.

Formation of ammonia from gaseous nitrogen and hydrogen has been found to be a non-chain reaction at low pressures and temperatures. The interest in this system has mainly centred on the effect of radiation in the heterogeneous and catalytic synthesis of ammonia, either in promoting energy transfer reactions or in lowering the thermal threshold of the thermal, equilibrium-limited synthesis.

Table 2. Experimental  $G$  values for exothermic reactions considered for radiation chemical processes<sup>1</sup>

Reaction	Product	Heat of reaction at 25°C, $\Delta H$ (kcal/mole)	$G_{\text{exp}}$ .	Type of radiation
$\frac{1}{2}\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) = \text{NH}_3(\text{g})$	Ammonia	-11.0	1	$\alpha$
$2\text{N}_2\text{O}(\text{g}) = \frac{3}{2}\text{N}_2(\text{g}) + \text{NO}_2(\text{g})$	Nitrogen dioxide	-47.3	5	F.F.
$\text{C}_6\text{H}_6(\text{l}) + \frac{1}{2}\text{O}_2(\text{g}) \xrightarrow{\text{Fe}^{2+}} \text{C}_6\text{H}_5\text{OH}(\text{l})$	Phenol	-1.9	1,000 <sup>6</sup>	$\gamma$
$n\text{C}_2\text{H}_4(\text{g}) = (\text{C}_2\text{H}_4)_n(\text{s})$	Polyethylene	-22.0	136,000 <sup>†7</sup>	$\gamma$
$\text{C}_6\text{H}_6(\text{l}) + 3\text{Cl}_2(\text{g}) = \text{C}_6\text{H}_6\text{Cl}_6(\text{l})$	Benzene hexachloride	—	85,000	$\gamma$
$\text{C}_2\text{H}_4(\text{g}) + \text{HBr}(\text{l}) = \text{C}_2\text{H}_5\text{Br}(\text{l})$	Ethyl bromide	-24.2	39,000 <sup>8</sup>	$\gamma$
$n\text{C}_2\text{H}_2(\text{g}) = (\text{C}_2\text{H}_2)_n(\text{s})$	Polyacetylene	—	75 <sup>†</sup>	$\alpha$
$3\text{CO}(\text{g}) = \text{C}_3\text{O}_2(\text{s}) + \frac{1}{2}\text{O}_2(\text{g})$	Carbon suboxide	—	2	$\alpha$
$2\text{RH}(\text{l}) + 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) = 2\text{RSO}_3\text{H}(\text{l})$	Alkane sulfonate	—	5000 <sup>9</sup>	$\gamma$

\*  $G_{\text{exp}}$  values for these reactions are in terms of number of reactant molecules converted to product per 100 eV absorbed.

Subscripts (l), (g) and (s) refer to liquid, gaseous, and solid state.

The radiation oxidation of benzene as a direct route to the synthesis of phenol has received some attention in connection with possibilities for a  $n, \gamma$ -chemonuclear reactor. Recent results<sup>6</sup> indicate that by the addition of metallic ions to an aqueous benzene solution while under the influence of a radiation field, the chain oxidation of benzene to phenol can be markedly increased at temperatures lower than those obtainable by purely thermal induction.

The radiation-induced halogenation of hydrocarbons has already reached commercial status in the form of the Dow process for the hydrobromination of ethylene<sup>8</sup>. It is understood that the chlorination of benzene for hexachlorobenzene production almost reached commercial status. However, this did not occur because of the problem of an insufficient market to support production from a new plant.

The sulphoxidation of long-chain hydrocarbons is receiving much attention and is reported to be near commercialization in connection with the production of biodegradable sodium alkane sulphonate detergents.

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Radiation polymerization of monomers is under investigation. One aspect of this subject is discussed in some detail below.

Certain reaction systems can be selected for a continued investigation because of their established importance to the overall economy. These systems may also be of value in generally advancing the research and development of chemonuclear and radiation chemical processing. In this respect, the following summarizes some recent work done at Brookhaven on the fixation of nitrogen for chemonuclear process development and the polymerization of ethylene in the field of radiation chemical processing.

Capsule irradiations of gaseous nitrogen-oxygen mixtures approximately equivalent in concentration to that of air have been carried out in the presence of a well defined fission fragment source inside a nuclear reactor<sup>10</sup>. The gas is subject to fission-fragment and reactor radiation which includes neutron and gamma radiation and proton radiation from the thermal neutron reaction with nitrogen. The absorbed dose is determined by gaseous nitrous oxide dosimetry. An estimate of the distribution of the various types of radiation energy can be obtained by means of independent flux measurements and gamma dosimetry, and this verified by analytical computation<sup>11</sup>. The development of improved methods of measurement of radiation energy within a reactor for inducing chemical reactions is a continuing requirement in this field. A typical yield or concentration build-up curve as a function of dose or energy absorbed is presented in *Figure 2* for nitrous oxide ( $N_2O$ )

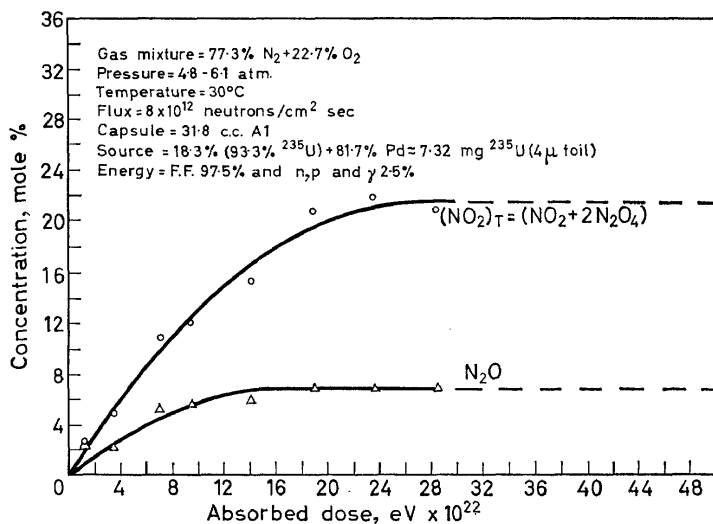


Figure 2. Fission-fragment and reactor irradiation (F.F., n, p and  $\gamma$ ).

and total nitrogen dioxide  $[(NO_2)_T]$  formation. The latter takes into account the association of nitrogen dioxide to nitrogen tetroxide. It is noted that a steady-rate concentration of about 21 mole per cent of total nitrogen dioxide and 6.9 per cent nitrous oxide is reached. The actual concentration of the higher oxide of nitrogen is distributed between 7.5 per cent associated nitrogen tetroxide and 6.3 per cent nitrogen dioxide by volume in the gas phase.

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Under conditions of 5–6 atm pressure and 30°C temperature, the partial pressure is not high enough for the nitrogen tetroxide to condense. At steady state, the nitrogen concentration is about 76.5 per cent and the oxygen is about 2.8 per cent, thus  $\approx 90$  per cent of the oxygen is converted to oxides of nitrogen. At higher pressures (up to 68 atm), the condensation pressure (about 1.5 atm) is reached, and the indications are that liquid nitrogen tetroxide condenses until the oxygen concentration in the gas phase approaches the above steady-state value. The steady state is not yet clearly understood, since competition exists between the initial species formed, which most likely includes nitrogen atoms, and the product nitrogen oxides and the necessary reactant oxygen. From an applied point of view, the more important feature of the curves in *Figure 2* is the initial slope, which indicates the maximum  $G$  values that can be expected. For the data shown, the initial  $G$  value for nitrogen dioxide,  $G_{1(\text{NO}_2)}$ , is 0.9, and that for nitrous oxide,  $G_{1(\text{N}_2\text{O})}$  is 0.6. For recovery as nitric acid, the higher oxides of nitrogen are of interest. *Table 3* lists the  $G$  values as a function of pressure up to 65 atm.

*Table 3.* Effect of pressure on initial  $G$  value for fission-fragment and Reactor Irradiation (F.F., n,p &  $\gamma$ ) of A  $\text{N}_2\text{-O}_2$  gas mixture

Pressure (atm)	$G_{1(\text{NO}_2)}\dagger$	$G_{1(\text{N}_2\text{O})}\dagger$	Radiation (per cent) (F.F.)	Energy Distribution (per cent) (n, p & $\gamma$ )
4.8	0.76	0.69	98.3	1.7
6.3	0.88	0.52		
17.0	1.20	0.41		
24.1	1.03	0.44	92.1	7.9
41.8	1.12	0.33		
51.8	1.28	0.26	81.3	18.7
64.8	1.21	0.27		

$\dagger (\text{NO}_2)_T = \text{Total NO}_2 = \text{NO}_2 + 2\text{N}_2\text{O}_4$ .

Gas mixture = 77.3 per cent  $\text{N}_2$  + 22.7 per cent.  $\text{O}_2$ .

Temperature = 30°C.

Neutron flux =  $1.1 \times 10^{13}$  neutrons/cm<sup>2</sup>/sec.

Capsule = 32.7 c.c. Al.

Source = 4  $\mu$  thick metal foil containing 5.04 mg <sup>235</sup>U, 18.3 per cent (93.3 per cent <sup>235</sup>U) + 81.7 per cent Pd.<sup>235</sup>

Time = 1 hour irradiation.

These are for one hour irradiations in the reactor; although not strictly initial values, they are close to the initial slopes of the yield-dose curves. These data are valid for a predominance of fission fragment radiation; the fraction of energy deposited by such radiation varies from 98.3 to 81.3 per cent because of the increased absorption of the reactor radiation, n,p and  $\gamma$ -radiation, as the gas pressure increased. The  $G_{1(\text{NO}_2)_T}$  values increase with pressure, but above 17 atm they seem to remain constant at a value of 1.2. The  $G_{1(\text{N}_2\text{O})}$  value in this interval decreases. These trends probably indicate the competition between nitrogen atoms and the oxygen reactant and nitrogen dioxide product. The same gaseous mixture was irradiated with reactor (n,p and  $\gamma$ ) radiation alone, and with pure <sup>60</sup>Co gamma radiation. A summary of the results is given in *Table 4*. The significant findings are as follows. (i) It is possible to build up relatively high concentrations of oxides of nitrogen in the gas mixture under the influence of radiation. This means



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that the economic feasibility of a radiation chemonuclear process for fixation of nitrogen may not be limited by the cost of recovery of product because of an insufficient nitrogen dioxide concentration. (ii) Under the conditions reported here, maximum  $G_{(\text{NO}_2)}$  values no higher than about 1.2 have been found. As will be discussed later, this means that the process is economically limited because of high energy requirements. (iii) Except for possible very low dose initial  $G$  values, there does not seem to be any significant

Table 4. Irradiation of a 77.3 per cent nitrogen + 22.7 per cent oxygen gas mixture. Temperature = 30°C

Radiation type	Initial Pressure (atm)	Initial $G$ values		Maximum measured concentration	
		$G_{(\text{NO}_2)_T}^\dagger$	$G_{(\text{N}_2\text{O})}$	Mole % $(\text{NO}_2)_T^\dagger$	Mole % $\text{N}_2\text{O}$
$^{60}\text{Co } \gamma$	5	0.9	0.6	0.6	0.4
	63	0.7	0.3	0.4	0.2
Reactor (n + p + $\gamma$ )	5	1.2	0.5	2.0	1.3
	66	1.0	0.05	2.0	0.1
Fission fragment and reactor (F.F. + n + p + $\gamma$ )	5	0.8	0.7	21.0 $\ddagger$	6.9 $\ddagger$
	65	1.2	0.3	24.4	3.7

$\dagger (\text{NO}_2)_T = \text{NO}_2 + 2\text{N}_2\text{O}_4$ .

$\ddagger$  Steady-state concentration.

difference in yield of nitrogen dioxide due to LET effects with different types of radiation. As the pressure is increased there appears to be a significant decrease in nitrous oxide yield under the influence of all types of radiation.

Even though the nitrogen-oxygen system has been under study for a number of years<sup>12</sup> much remains to be done to achieve a fuller explanation of the radiation chemistry and to improve the yields. In addition to theoretical considerations, recent radiation-induced exchange reactions between nitrogen-14 and nitrogen-15 isotopes indicate an initial  $G$  value for nitrogen radical formation of 11.5<sup>12, 13</sup>, which possibly fixes an upper limit for the  $G$  value of nitrogen dioxide formation. Determination of the yield-dose build-up curves for evaluating initial  $G$  values and steady-state concentrations over the complete range of nitrogen-oxygen concentrations are needed to establish precisely the kinetics and the competition between reactants and products. Investigation of the effect of pressure ranging up to several thousand atmospheres at low oxygen concentrations and in the presence of water, as suggested by extrapolation from some exploratory experiments of Hardeck and Dondes<sup>12</sup> and Dmitriev and Pshchetskii<sup>14</sup>, could prove interesting. Experiments at temperatures up to 1500°C for determining the effect of radiation on the thermal yield of nitric oxide could also prove attractive. This is suggested on the basis of some recently reported experiments of Dmitriev and Sorokin<sup>15</sup> in which the radiation yield is found to be enhanced at temperatures in the range 700–1000°C.

With regard to the development of fission-fragment radiation sources

and chemonuclear fuel elements, the problem is to develop a fuel that is thin enough to give a significant energy deposition efficiency while at the same time having good radiation, chemical, thermal, and fluid dynamic stability. Stationary metal foil sources have been preferred to ceramic and dynamic (dust or gaseous) sources because of their stability and higher thermal conductivity. The fission fragment sources used in the experiments mentioned above consisted of a  $4\mu$  thick foil of an alloy of 18.3 per cent fully enriched uranium in solid solution with palladium yielding a fission-fragment efficiency of  $\approx 25$  per cent. This alloy was chosen primarily because of its high malleability which allows it to be cold-rolled into thin sections. Foils as thin as  $2.5\mu$  yielding an efficiency of 50 per cent have been produced. It has been found that at higher nitrogen dioxide concentrations, in a radiation field, the uranium-palladium alloy may be severely attacked. This is thought to be due to a reaction between the protective oxide layer formed on the bare uranium-palladium surface and the nitrogen dioxide, which is accelerated in the radiation field. Coating the foil with an extremely thin layer of platinum has solved the problem. This procedure markedly reduces the corrosive action and provides a buffer for reducing loss of uranium due to possible evaporation in the process of emission of fission fragments. Since the protective layer is submicron in thickness, it absorbs a relatively small fraction of the energy of the fission fragment passing through it. An effective method of arranging a foil of this thinness for reactor purposes is in a honeycomb array. In this manner dimensional stability under high gas velocities can be achieved. Assemblies fabricated for demonstration purposes using  $2.5\mu$  thick metal foil are shown in *Figure 3*. Adjustments of energy deposition efficiency is obtained by varying the size of the individual cells in the honeycomb as shown.

A chemonuclear in-pile research loop is under construction at Brookhaven for study of the radiation chemistry and the fuel problem in a flowing system. With this loop which is, in effect, a small pilot plant, attempts will be made to determine the extent of the radioactive contamination of the oxides of nitrogen produced.

Turning to the question of where we stand concerning the economic evaluation of a chemonuclear nitrogen fixation process, in addition to the studies already performed<sup>16, 17</sup>, a basic analysis can be made in terms of a comparison of the critical item of unit energy requirement for competitive methods of fixing nitrogen. This comparison is made in *Table 5*. The competitive method is the synthesis of ammonia in an electro-chemonuclear system. Hydrogen, produced in efficient water electrolyzers using d.c. electrical energy generated by a nuclear reactor, can be combined with nitrogen separated from air by liquefaction, in the conventional high pressure catalytic process for ammonia synthesis. The equivalent  $G$  values and thermal energy requirements calculated by using presently available efficiencies in low and high pressure electrolytic cells, combined with present average and maximum values for power cycle efficiency, are given in *Table 5*. At a  $G$  value of 1 for the fission-fragment system, the energy requirement is very high. At the present maximum experimental  $G$  value of 6, the energy requirement is still 1.5 to 2.7 times as high as those for the electrolytic systems. It is only at the kinetic maximum of 11.5 that

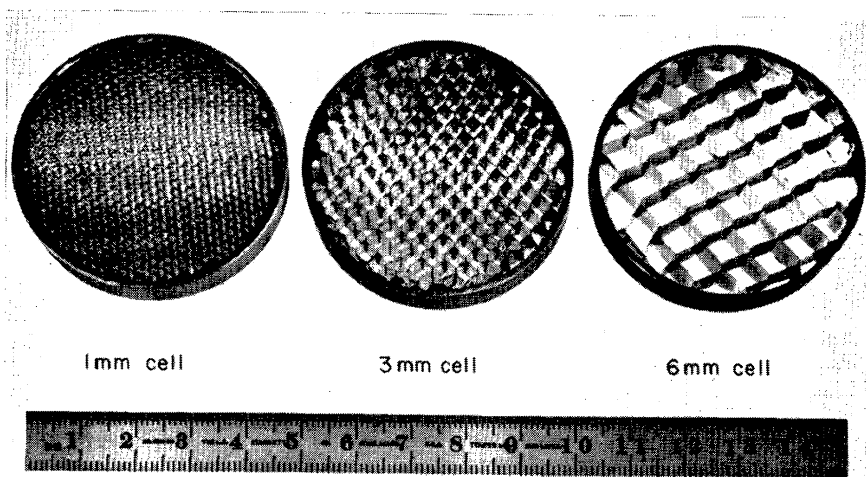


Figure 3. Honeycomb assembly of 2.5  $\mu$  foil for fissio-chemonuclear element

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the fission-fragment system begins to look competitive. Although there may be some advantage in plant cost for a direct fissio-chemonuclear synthesis plant, the conclusion is that with the present state of knowledge it is difficult for the process to compete on the basis of producing nitrogen dioxide alone, which is referred to as a single purpose plant. However, by combining a fissio-chemonuclear system with power production in a dual-cycle system, as shown in the bottom section of *Table 5*, a *G* value of 6 or a net *G* value of

*Table 5.* Comparison of energy requirement for fixation of nitrogen using nuclear energy

<i>Process</i>	<i>G-value for N fixation</i>	<i>Energy deposition efficiency</i>	<i>Net G-value for N fixation</i>	<i>Thermal energy required kWh/lb.N</i>
<i>Fissio-chemonuclear synthesis of NO<sub>2</sub> from atmospheric N<sub>2</sub> and O<sub>2</sub></i>				
BNL experimental value	1.0	50	0.5	174.0
Maximum experimental value	6.0	50	3.0	29.0
Kinetic maximum	11.5	—	—	7.6
Thermodynamic maximum	284.0	—	—	0.31
<i>Electro-chemonuclear synthesis of NH<sub>3</sub> by catalysis of electrolytic H<sub>2</sub> and atmospheric N<sub>2</sub></i>				
Low pressure cells (65 per cent efficiency)	14.7	30†	4.4	19.8
High pressure (85 per cent efficiency)	19.2	42†	8.1	10.8
<i>Dual cycle synthesis combines electro-process at 10.8 kWh/lb.N with the Fissio-process at the indicated G-value</i>				
	1.0	50	0.5	10.2
	6.0	50	3.0	7.8
	11.5	—	—	4.5

† Thermal to electrical power generation efficiency.

3 would probably be economically attractive. The total energy requirement at this condition could decrease to 7.8 kWh/lb. of nitrogen fixed and would then be about as low as the thermal equivalent of natural gas now being used to a large extent as the conventional source of energy and raw material for ammonia production. The dual-cycle system is shown in *Figure 4*. At a net *G* value of 3, 27 per cent of the nitrogen would be fixed as nitrogen dioxide directly in the reactor at temperatures high enough to generate power for production of electrolytic hydrogen which would be used in fixing 73 per cent of the nitrogen as ammonia. It thus becomes necessary to determine the radiation yields at temperatures, above about 500°C, at which condition it is most economic to convert thermal to electric power. The economics can be further improved in conjunction with large integrated multi-purpose plants which would produce fixed nitrogen and electrolytic oxygen in addition to desalinated water and power. Although an engineering scale experiment has not as yet been found justified, there is ample incentive for continued research and generalized development for a chemonuclear nitrogen fixation process.

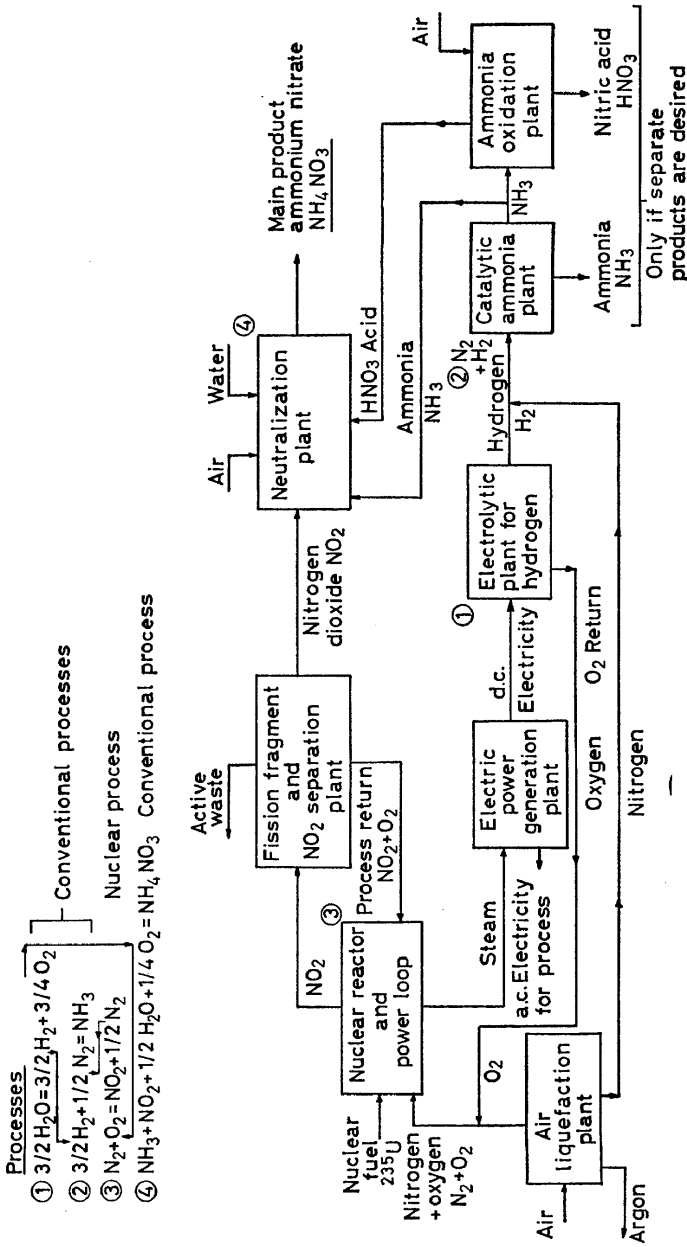


Figure 4. Dual-cycle fissio- and electro-chemonuclear system for nitrogen fixation.

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In the case of radiation chemical process development, polymerization reactions have been found to be effectively induced by isotopic and machine radiation sources. The availability of large inexpensive raw material supplies of ethylene monomer and the rapidly expanding market for polyethylene provide an incentive for developing a radiation-induced polymerization process. Studies on the  $^{60}\text{Co}$  gamma radiation induced homopolymerization of ethylene has revealed the following<sup>7, 18, 19</sup>. Polymerization at temperatures below the melting point of the polymer can be inhibited by oxygen. The rate of polymerization increases as a strong function of the pressure. The rate increases approximately with a fractional power of the radiation intensity. The kinetics are thought to be predominantly controlled by a free-radical chain mechanism with a bi-radical chain termination step. The kinetic mechanism is complicated by the heterogeneous nature of the system. There is little effect of temperature on rate when producing solid polymer at temperatures between 20° and 100°C, the activation energy being <2 kcal/mole. The rate increases rapidly at temperatures above 120°C when producing liquid polymer. The activation energy is about 14 kcal/mole between 120° and 200°C. The two main problems involved in applying a radiation process for polyethylene synthesis are to obtain a rate high enough to compete with conventional thermocatalytically-induced processes and to produce a polymer which has market acceptability. Some recent results<sup>20</sup> at the limits of experimental conditions performed at Brookhaven are shown in *Table 6*, together with the rate and *G* value equations de-

*Table 6.*  $^{60}\text{Co}$  Gamma radiation induced polymerization of ethylene. Results at limits of experimental conditions in static capsule experiments

Intensity (rad/h)	Pressure (atm)	Average Temperature (°C)	Conversion (per cent.)	Differential values	
				Rate, <i>Q</i> gm/l./h	<i>G</i> value mole/100eV
182,000	1920	21	8.0	593	189,000
847,000	680	32	70.5	780	64,000
179,000	850	200	13.1	2,870†	1,130,000

† Run terminated by decomposition reaction.

Rate and *G* Value Equations

For Range Temperature = 20–100°C

Pressure = 170–1360 atm

Intensity =  $(0.58-8.5) \times 10^5$  rad/h

$Q = 1.39 \times 10^{-8} e^{-200/RT} p^{2.7} \pm 27$  per cent

$G = 3.5 e^{-200/RT} p^{2.5} I^{-0.5} \pm 27$  per cent

For temperature range of 120–200°C, Activation energy  $E = 14,500$  kcal/mole.

veloped for a constant volume non-flow system. The differential values have been determined from yield-dose curves. These data indicate that for production of solid polymer at low temperatures, differential rates ranging up to 1 g/l./h per atmosphere of ethylene pressure with *G* values in the tens to hundreds of thousands may be obtained. For the liquid phase, rates ranging into the thousands of g/l./h and *G* values into the millions may be obtained. In fact, rates that were sufficiently high to cause thermal decomposition were encountered in these experiments. These rates and *G* values begin to appear interesting for use in developing an economic process. For example,

at a  $G$  value of a million it takes only 40,000 Curies of  $^{60}\text{Co}$  to produce 50 million lb./year of polyethylene. These values must, however, be confirmed in a continuous-flow type experiment before they can be taken seriously. The type and quality of polymer produced depend on a combination of the conditions of temperature, pressure, and intensity used in the synthesis. Indeed, there may be two different processes possible with radiation, one for the solid phase and the other for the liquid. Below the melting point and up to 680 atm, the polymer tends to be of intermediate density (0.935–0.95) and to have characteristics of a non-crosslinked long-chain linear polymer. Above the melting point, at temperatures of  $150^\circ\text{C}$  and pressures of 680 atm and above, the polymer tends to be of lower density and to have a lower molecular weight and a higher melt flow characteristic not unlike commercial grade low density polyethylene. Among the possible advantages of a radiation process are: (i) the elimination of catalyst impurity fractions which could alter some of the properties of the polymer, (ii) a more convenient and precise method of controlling polymerization rate and altering product quality and (iii) a reduction of circulating gas requirement by going to higher conversions per pass. Radiation polymerization vessel design studies<sup>21, 22</sup> have been made to show the optimization between vessel volume and the quantity of  $^{60}\text{Co}$  gamma radiation required. Because of the high pressure, density, and volume conditions,  $^{60}\text{Co}$  gamma radiation is preferred to high voltage machine radiation. Further design and pilot plant studies are needed to solve the heat and mass transfer problems involved<sup>23</sup>. It can be shown that the cost of producing a free radical by means of radiation is about equal to that of one formed by means of a peroxide chemical catalyst. It should be possible to develop a process which is at least as economical as the conventional process, thus providing an alternative for the expanding polyethylene economy.

Probably of greater interest to polymer chemistry are studies on the copolymerization of ethylene with other monomer compounds.  $^{60}\text{Co}$  gamma radiation induced copolymerization provides advantages at conditions of temperature and pressure not readily obtained by means of thermocatalytic methods. Survey studies at 680 atm and  $20^\circ\text{C}$ <sup>24</sup> have established that high molecular weight copolymers of ethylene can be formed with the vinyl chlorides, acetates, alcohols, ketones, and benzene monomers and with substituted ethylene, propylene, butene, sulphur dioxide and carbon monoxide monomers. More detailed studies have been made with the ethylene-carbon monoxide system<sup>25–27</sup>. The kinetics of the system have been found to be extremely interesting. At  $20^\circ\text{C}$  and 680 atm, concentrations up to 1 per cent carbon monoxide retard the polymerization of ethylene; increasing concentrations of carbon monoxide produces an increase in copolymerization rate, which reaches a maximum in the range of 30–40 per cent carbon monoxide, and at still higher carbon monoxide concentrations, approaching pure carbon monoxide, the rate decreases to low values<sup>25</sup>. *Figure 5* shows a phase diagram of copolymer composition versus initial monomer gas composition. The system is highly non-ideal. An azeotrope exists at 48.5 per cent carbon monoxide. Copolymers containing  $> 50$  per cent carbon monoxide as well as polymers of carbon monoxide alone have been formed. Here an important kinetic point is that in the concentration range of 8–40 per cent carbon monoxide at  $20^\circ\text{C}$  the rate of addition of carbon monoxide to

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a free-radical polymer chain-end is 23.6 times as fast as that of ethylene. This reactivity ratio decreases with increasing temperatures. As shown in Figure 5, polymerization with conventional catalysts requiring higher temperatures for initiating polymerization does not yield polymer compositions

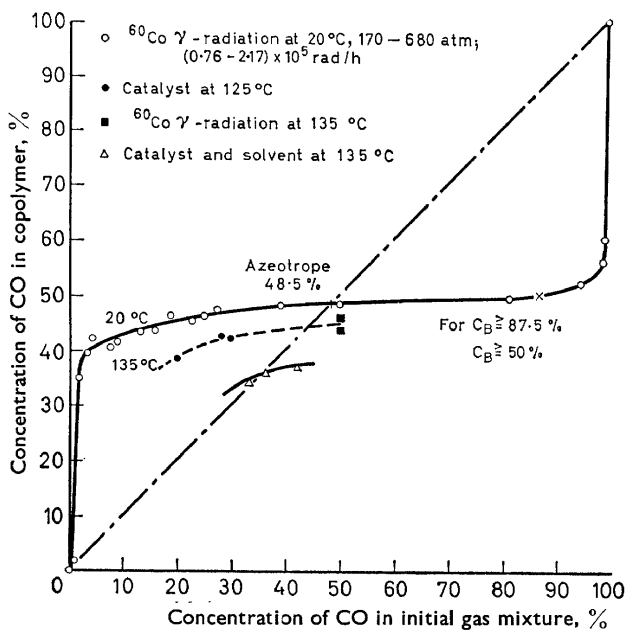


Figure 5.  $^{60}\text{Co}$  gamma copolymerization of ethylene and carbon monoxide

that can be obtained with radiation at lower temperatures. The data in the literature<sup>28</sup> indicate a low molecular weight wax, while the polymer produced at a lower temperature under the influence of radiation gave a high molecular weight solid polymer. The properties of the copolymer are strongly affected by the polymer composition. The density increases linearly from 1.07 to 1.25 as the concentration increases from 31 to 50 per cent carbon monoxide; over the same range, the crystalline melting point increases rapidly from 111° to 242°C. These results indicate that work with radiation can conveniently yield experimental results leading to a better understanding of copolymerization kinetics and can open up the possibility of producing useful copolymers with inexpensive raw materials. The recent interest in *in situ* polymerization of monomers in wood<sup>29</sup> may be considered as a special case of radiation copolymerization.

This report has surveyed, in a relatively brief manner, only those systems best known to the author from his work in the development of large-scale radiation chemical synthesis. Unquestionably other interesting and important developments might be mentioned, including the use of radiation in lowering the thermal threshold, improving the specificity of hydrocarbon cracking<sup>30</sup> and in partial oxidation reactions, and radiation effects in heterogeneous systems from the point of view of improving the utilization of high



energy radiation as well as improving product specificity. There is a trend toward initial use of high energy radiation in complementing conventional methods of processing, with consequent improvement in conditions of temperature and pressure, and in complementing different types of catalysts in existing processes. This is a continuing development, more of which we shall certainly be made aware of in the papers presented at this Congress.

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