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Beta Radiation Processing at Rigorous Conditions *

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Introduction

The literature reflects ever expansive studies of radiation chemistry over the past twenty years. However, in the application of radiation processing to chemical reactions, in general and excepting a few isolated cases, the yields of useful products have been so low as to preclude practical utilization. Thus, for many reactions, radiation alone at ambient conditions is not a sufficient agent for economical production. Hence, we are led to the investigation of radiation effects on reactions at elevated temperatures and pressures where the thermodynamics favor more extensive reactions that may be induced by radiation. The probability of developing a successful practical radiation process is increased when applying radiation at rigorous conditions. To have a commercial advantage, a radiation process usually must replace an expensive catalyst system, generate a reaction at somewhat less rigorous conditions than is usually employed or yield a better or unique product of high value. In our investigations, we have examined only the potential of radiation as a replacement for contact catalyst.

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For radiation processes at high temperatures and high pressures, beta ray sources inside the chemical reactors have distinct advantages over the other forms of radiation, as gamma, accelerated electrons and hard X-rays. Internal beta sources afford a high level of radiation in the reaction zone from a relatively small source. More than a hundred times as many curies of a gamma emitter, as Co-60, would be required to give the same useful radiation dose rate as obtained from an internal beta source. This is because beta rays deposit the bulk of their energy along a short path inside the reactor where it is needed, as opposed to gamma rays which wastefully dissipate their energies over long ranges in surroundings, with but a small fraction of the energy being applied in the reactor where needed. Another advantage of beta sources follows as a corollary. That is, with most of the radiation retained within the reactor, the shielding problem is greatly reduced. The only external radiation is a relatively minor amount of Bremstrahlung radiation that arises from the decelerating beta rays in the reactor. The Bremstrahlung radiation usually does not require extra shielding other than the metal structure of the reactor itself. The advantages over machine generated radiation are clearly that electron beams from an accelerator cannot at all penetrate inside high pressure vessels or reactors and machine X-rays either dissipate most of their energy in surroundings like gamma rays, if they are hard, or suffer serious attenuation by reactor walls if they are soft. Also machine X-rays would require massive shielding.

Radiation Processing Apparatus

The radiation processing unit, shown in Figure 1 is basically a high pressure, high temperature reactor for bench-scale experiments, in which beta radiation directly replaces contact catalysts. The unit is designed for operations to 10,000 psi and 500°C for either liquid, vapor or mixed phase reactions. The cylindrical reactor wall is 2-inch thick stainless steel. This is enveloped by a 2-inch thick aluminum electrical heating jacket and 2-inch thickness of magnesia insulation. This assembly is within a 2-foot diameter, 3/8-inch thick steel containment cell for protection against area contamination in case of a high pressure rupture. The source shown consists of 90 curies of Sr-90, Y-90, in the form of Minnesota Mining and Manufacturing Company's (3M Brand) radiating ceramic microspheres, sealed within 485 hollow stainless steel needles that are cross-stacked within the reactor. Chemical reactants are irradiated by mixing through the interstices of the stack of needles by a magnetically driven recycle pump. The reactants are initially pumped into the reactor.

Strontium-90 was the pure beta emitter of choice for the source because of availability, relatively low cost and the 2.2 mev beta ray from the daughter isotope, Y-90, can penetrate the 4 mil steel walls of the needles. 3M Brand radiating microspheres was chosen as the form of radioactive material because of high temperature stability and it is relatively chemically inert and insoluble. The latter two are desirable properties in case of source leakage.

For this particular 90 curie source inside the assembly shown in Figure 1, the Bremstrahlung radiation at the outer surface of the containment cell was 30 mr/hr. At the normal operating area at the control panel about two feet from the cell, the radiation is well below 5 mr/hr. Usually, the operator was exposed to no more than 1 mr/hr, illustrating the safety and ease with which high intensity radiation experiments can be conducted by using beta sources.

In order to be able to determine the G-values (number of molecules reacting per 100 ev of radiation energy) for observed future radiation reactions, it is necessary to know the radiation dose rate in the reactor space. Dosimetry was first attempted by the Fricke method(1,2), i.e., radiation induced oxidation of ferrous to ferric ions in dilute sulfuric acid. This system did not work in the reactor due to reaction between the reactor steel walls and the acidic solution. Dosimetry tests with aqueous solutions of methylene blue(2) likewise behaved abnormally, likely due to reactor wall effects.

Successful dosimetry for the 90 curie source was accomplished with the non-aqueous iodine-heptane system, using procedures described in reference(3). The basis of dose measurement is the formation of free radicals from the heptane, followed by rapid combination of the radicals with iodine. The technique employed was to measure the molecular iodine depletion from irradiated iodine-heptane solutions as a function of exposure time. As presented in Figure 2, the expected linear depletion rate(3) is observed when the heptane is pre-purified of traces of reactive compounds by a preliminary reaction with iodine in the irradiator reactor until the molecular iodine is completely used up. Another iodine solution is then made with this radiation purified heptane for the dosimetry measurement. Initial iodine concentrations were 0.4 milligrams per ml of heptane. Iodine concentrations were measured with a spectrophotometer at 520 mμ wavelength, where the molar extinction coefficient for iodine is 859.

Based on a G-value of 3.4 for iodine molecules absorbed upon irradiation of the heptane solution(3), the following dosimeter relationship is easily derived,

$$R = -1630 \times 10^{3} \frac{\text{rad}}{\text{hr}} \times dc/dt \qquad (1)$$

where c is iodine concentration in grams/ml, t is exposure time in hours and R is the radiation dose rate in rad/hr.

The dosimetry measurements shown in Figure 2 yield the mean radiation dose rate within the reactor space equal to 0.98×10^{6} rad/hr. This is the rate of radiation energy dissipated throughout the 100 ml of reactant liquid in the reactor. During irradiation, most of this liquid is in the interstices between the cross-stacked tubular needles that contain the radioactive material.

It is of interest to determine the efficiency of this source design for getting the beta radiation energy into the reactant volume for processing. Taking an average of 10^6 ev of energy per disintegration, one obtains 12.0×10^{21} ev/hr from 90 curies. From the dosimetry measurement, the 0.98×10^6 rad/hr converts to 4.16×10^{21} ev/hr absorbed in 100 ml of liquid having a density of 0.684. Thus, the radiation utilization efficiency for this beta source design is 4.16/12.0 or 34.7%. Similar calculations for gamma sources, for the useful fraction of overall radiation absorbed in reactor volume, is several orders of magnitude less. Thus, internal beta sources have a definite economic advantage over gamma sources which must have of the order of more than 100 times as many curies to supply the same useful radiation field.

Twenty high pressure, high temperature experimental runs (to 5000 psi at 430°C) were conducted with the cross-stacked needle source before slight leakage was observed by monitoring Geiger counters situated on the product lines from the reactor. Source disassembly revealed that the needles were flattened by the pressure operations. It is suspected that flexion of the thin metal walls on pressurizing and depressurizing led to stress-corrosion and eventually some cracking near the more rigid welded ends, permitting leakage of the 70 micron microspheres.

A new beta source is currently under construction, designed to better withstand the operational specifications of 5000 psi at up to 500°C. This source is made by swaging stainless steel tubing over granulated strontium-90 titanate, forming a very hard compaction inside a tight metal sheath. Swaging reduces the tubing diameter to 70% of the original packed tube diameter. The compaction completely supports the thin metal wall against flexion under pressure which might lead to strains and rupture. Thorough leak testing of mock-up sources of coiled swaged tubes, containing non-radioactive strontium titanate has proven that this source design satisfies the above specifications, and no deformation and no leakage occurs at reaction conditions.

Solid strontium titanate is the chemical form of radioactive material to be used for this source because it is chemically inert, stable at elevated temperatures and has the proper compaction properties for swaging. The presently planned source will be a single coiled tube, 13 ft. long, 64 ml diameter with a 5 mil wall thickness. It will contain 500 curies of strontium-90 titanate. There will be only two welded ends for the single tube source which will be coiled to fit within the present reactor. Because of the high specific activity of the radioactive material (32 curies per gm), higher total activity and improved source geometry, it is expected that 5 to 10 megarad/hr dose rate will be available in the reactor.

Results

Most of our radiation processing investigations so far have been on the evaluation of beta radiation as a catalyst for hydrogenation of coal extract (50-80% of coal). This hydrogenation reaction is of prime interest because such conversion of coal, or gross derivatives like extract, to liquid fuels could open up vast new markets for the coal industry, provided an economically competitive process can be developed. If it could be demonstrated that radiation would promote hydrogenation sufficiently for radiation to replace relatively expensive contact catalyst, then the economics of the conversion process might be improved.

We have worked with coal extract rather than coal because it can be melted or dissolved to facilitate pumping into the processing unit and, in general, permits easier handling than a solid. From numerous radiation runs with coal extract in the liquid phase, treated with 5000 psi of hydrogen pressure, temperatures up to 430°C, and total dose of up to 6 megarad, we have disappointingly but conclusively observed that radiation does <u>not</u> induce hydrogenation beyond that obtained by thermal reaction alone. That is, the hydrogen content of the gross products is no greater than for comparative runs with no radiation and with no catalyst. In confirmation of this, we have found no addition of hydrogen to the aromatic bonds in coal model compounds, as methylnaphthalene and biphenyl, which were treated under similar processing conditions. (Coal is largely aromatic in chemical structure, hence the aromatic model compounds.) Thus, it seems definite that radiation does not promote hydrogenation of aromatic bonds to a practical amount.

However, in spite of no significant increase in hydrogen addition to the overall coal extract products, there was observed an improved yield of 100 x 400°C boiling oils from radiation runs of 2 hour duration, at the lower pressure of 1000 psi of hydrogen. Occasionally, isolated pairs of radiation vs. non-radiation runs indicated markedly improved yield with radiation. However, after sufficient comparative runs were completed to check the radiation yield and to obtain statistically significant averages for such complex products as from coal extract, it was found that the benefit of radiation in yield of distillable oils from extract was marginal. Comparative hydrogenation tests were made at reaction times varying from 1 to 6 hours, at 430°C. Averaged data from the distillation of the products from the runs, yielded the curves shown in Figure 3. The difference in the curves, from 2 to 4 hours is statistically significant since the probable error is ± 1.3% yield. Note that the radiation and non-radiation curves reach the same asymptotic limit at 6 hours reaction time. It is likely that radiation is promoting only the rate of thermal hydrocracking of the extract and doesn't extend the limit of cracking that would ultimately occur by thermal radiation alone. This small radiation induced acceleration of hydrocracking alone is not deemed commercially attractive.

In the course of examining extract hydrogenation products (oils), it was regularly observed that the 100° x 400°C boiling oil products from hydrogenation-radiation runs had much less of the unwanted hetero atoms, N, S, than the products from non-radiation runs. Relevant data are tabulated in Figure 4.

Removal of N and S from heavier hydro-oils is essential for subsequent catalytic cracking to lower weight gasoline fractions. Cracking catalysts are easily poisoned by N and S. Thus, the hydrorefining of oils as derived from extract by conventional catalytic hydrogenation will be further investigated with the new source, as a promising application of radiation processing. These oils, as opposed to extract, will be radiation-hydrogenation processed in the vapor phase since it is expected that such radiation induced chain reactions are more extensive in the vapor phase. Also, the radiation induced hydrocracking of oils in the vapor phase is expected to be more extensive than the observed hydrocracking of extract. The possibility will be examined that both the hydrorefining (removal of Nand S) and the hydrocracking of coal-hydro-oils to lower molecular weight oils may be combined into a single step radiation process.

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PMY:rmc
Attachments:
Figures 1, 2, 3 and 4

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FIG. 1

MODIFIED SR-90 HYDRO REACTOR

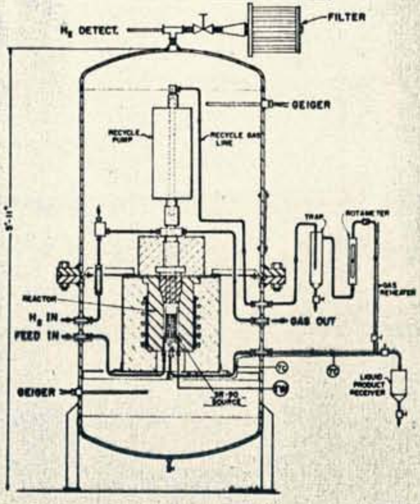

FIGURE 2

IODINE-HEPTANE DOSIMETRY OF THE RADIATION PROCESSING REACTOR

$$\text{Dose Rate} = -1630 \times 10^{6} \frac{dc}{dt} \left(\frac{\text{Rad.}}{\text{Hr.}} \right)$$

c= gms/ml of I in Heptane.
t= Hours.

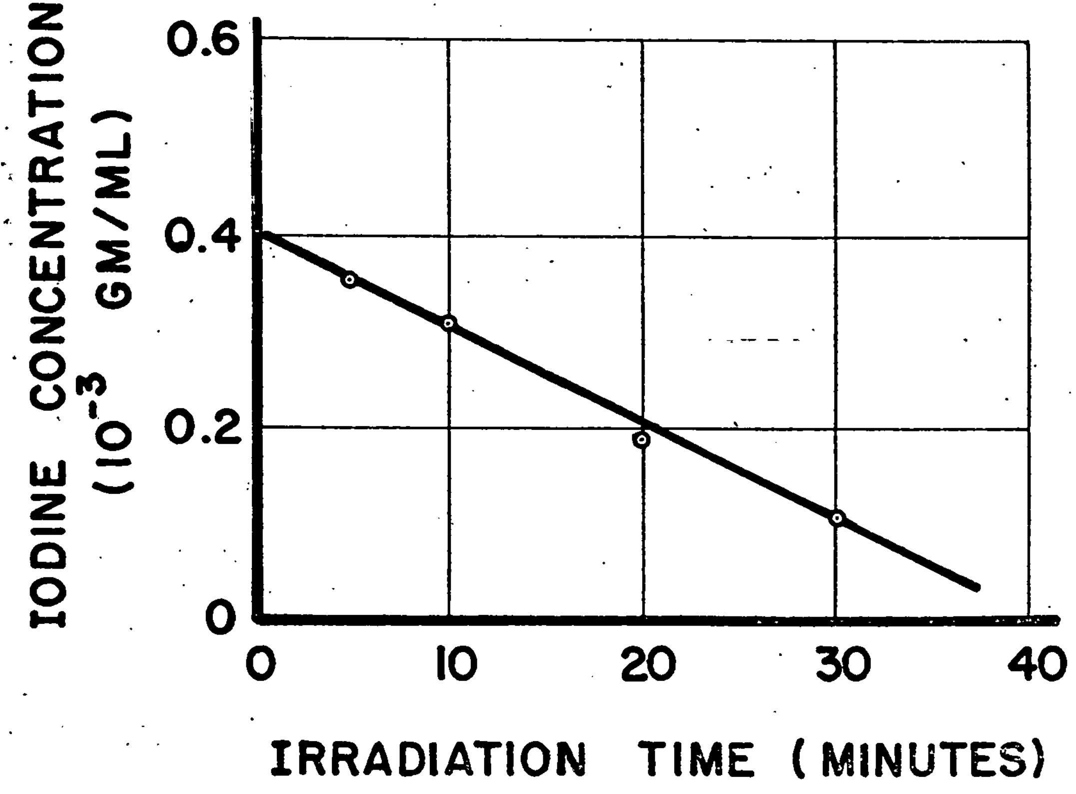

FIGURE 3

EFFECT OF RADIATION ON YEILD OF HYDRO-OIL FROM COAL EXTRACT

0.98 MEGARAD /HOUR

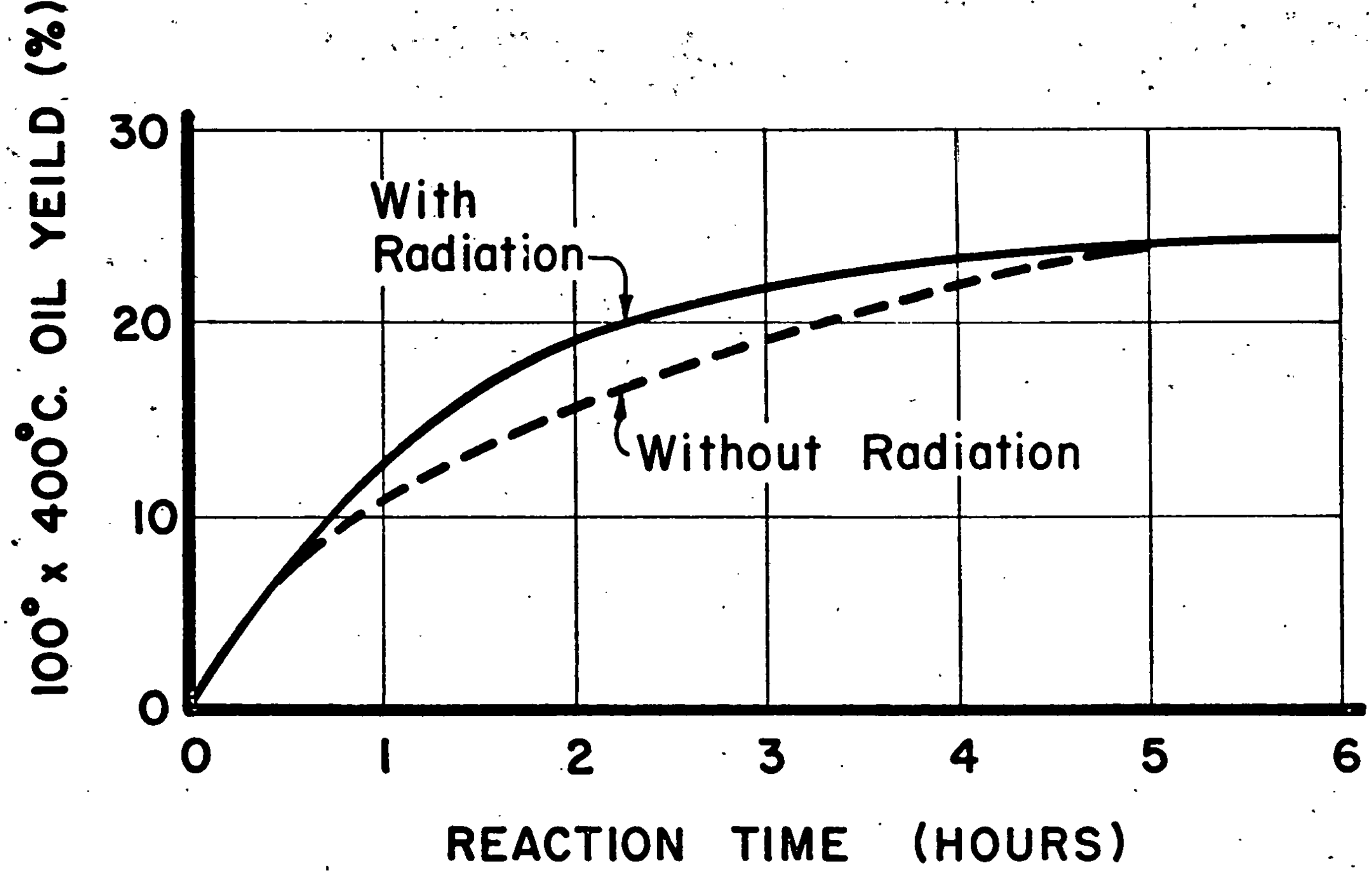

FIGURE 4

RADIATION INDUCED REDUCTION OF N & S IN -400°C. DISTILLATE FROM HYDROGENATED COAL EXTRACT

CATALYST	HYDRO RUN TEMP.	REACTION H_2 SATURATED	% N	% S
NONE	429°C.	YES	0.20	0.20
0.98 MEGARAD	429°C.	NOT LIKELY	0.14	0.11
0.98 MEGARAD	429°C.	YES	0.06,0.08	0.06,0.06
NONE	389°C.	YES	0.10	0.14
0.98 MEGARAD	389°C.	NOT LIKELY	0.06	0.08
0.98 MEGARAD	389°C.	YES	0.0,0.02	0.02,0.07