

Irradiation of Biomass: Need, Importance, Science and Technology

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Abstract

Biomass can play a significant role in reducing our energy dependence on conventional fuels and also in bringing the prices of food commodities down. Preventing environmental pollution is another benefit of biomass derived fuels. Lignocellulose complex is the major constituent of biomass. While several treatments are available for converting cellulose present in biomass to simpler fermentable sugars, none is effective alone. To alleviate the problem of environmental pollution associated with high doses of chemicals required for chemical treatments, irradiation can be an efficient treatment along with high temperature and chemicals. Irradiation causes a breakage in the structure of cellulose by causing rupture of 1,4- β -glucoside bonds and some glucopyranose rings. Several combinations of treatments have been developed with varying degrees of conversion efficiency. We need a more directed and collaborative effort toward improving the efficiency of irradiation for converting biomass to fermentable sugars.

Introduction: Today's world is dependent for its energy requirements on oil and coal. While these resources are non-renewable, other issue of major concern are soaring prices and business cartel of countries which are major producer of these. We can not assume a growing world without its energy requirements being met.

While the reserves of coal can last another century and we have its alternatives to produce electricity e.g. nuclear energy, solar energy, we don't have many alternatives for gasoline to run our automobiles. This can put the world's progress in jeopardy if we don't come up with sustainable and practical ways to mitigate this problem. Another important factor in developing alternative fuels is to prevent channeling of food (corn grains and other starch rich produce) to produce ethanol and other resources.

Lignocellulosic Biomass: Biomass refers to living and recently dead biological material that can be used as fuel or for industrial production. Here in the paper biomass means Lignocellulosic biomass – it is a complex polymeric network of cellulose, hemicellulose, pectin and lignin.

Importance: Usage of biomass can address these problems in several ways. As defined previously, biomass is a dead biological material. It is either dumped to be degraded naturally or it is used as a fuel with low energy conversion efficiency. Developing fuel from biomass (ethanol or precursors of gasoline) will

help in reducing the dependence on conventional fuel sources as it can be blended with the gasoline. It will help in reducing the prices of food commodities since it can be a cheaper method of producing ethanol than starchy foods. This will reduce the environmental pollution also as the biomass is not dumped or used as an energy source directly in its raw form.

The primary requirements are to develop a cost effective technology to convert lingo-cellulose to ethanol or other fuel sources and to develop an infrastructure and tax benefit system to promote the usage of biomass for biofuel generation. (Wyman, C. E., 1994)

Cellulose: At the present time, the generally accepted approach regards cellulose as a material with a crystalline structure containing quantities of an amorphous phase. Different models of the crystallographic lattices of cellulose and theories of the crystallinity of this polymer exist. The length of the polymer chains is appreciably greater than the size of the crystallites, so that the macromolecules are present in alternating regions with crystalline and amorphous structures. The complex amorphous-crystalline system can be characterized by the degree of crystallinity and the degree of orientation. The crystalline phase is more closely packed, so that the rates of hydrolytic splitting differ considerably for this phase. (Ershov, B. G., Klimentov, A. S., 1984).

Each monomeric unit in cellulose has three hydroxyl groups, which form intra- and intermolecular hydrogen

bonds. The presence of the branched system of hydrogen bonds determines to a considerable extent the physicochemical and mechanical properties of the polymer.³ The cellulose macromolecule includes D-glucose repeat units, joined by 1,4- β -glucoside bonds.

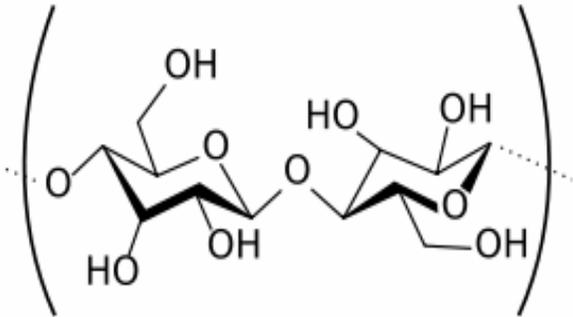


Figure1. Organizational structure of Cellulose

Sources of Biomass: Common examples of Lignocellulosic biomass include agricultural and forestry residues, the paper and much of the remaining organic fraction of municipal solid waste (MSW), industrial processing residues such as wastes in the paper and pulp industry, and herbaceous and woody plants grown as feed stocks for the production of fuels. (Wyman, C. E., 1994; Wiselogel, A., Tyson J., Johansson D., 1996)

The major polymers present in biomass are cellulose, hemicellulose and lignin. Cellulose is a polymer of thousands of glucose units joined together by the beta 1-4 glycosidic bonds. This polymer is 35-50% of the Lignocellulosic biomass and this is the polymer which we want to convert back to glucose for fermentation. The second major compound is hemicellulose which contributes 20-35%. The composition of hemicellulose varies depending upon the source. Xylose, a pentose sugar is the major monomeric unit of hemicellulose. Lignin contributes 15-25% of the lignocellulose. It's a phenyl propene polymer and has very complex composition. It can not be broken down to produce smaller sugars.

How biomass is converted to biofuel – As discussed previously, to convert biomass to bioethanol, we need to treat biomass. The cellulose present in the biomass degrades down to glucose or other simpler sugars. Also, the hemicellulose can be degraded down to Xylose. These sugars can be fermented using bacteria or fungi to produce ethanol.

Need for pretreatment: The components of Lignocellulosic complex make a network like structure. This network is very tightly bound and doesn't allow the enzymes (cellulase, cellobiase) to reach the inner

sites of the complex where cellulose is present. This results in a very low conversion rate of cellulose to simpler, smaller fermentable sugars. The crystalline structure of cellulose is another major factor resulting in low sugar conversion ratio.

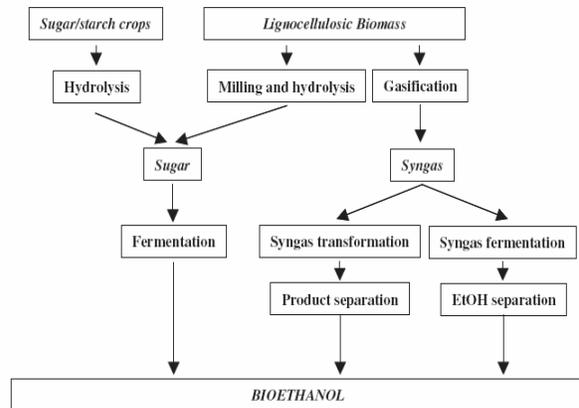


Figure 2: Different ways bioethanol is produced. (Adopted from Chiaromonti, D. *Bioethanol: Role and production technologies*, P. Ranalli (ed.), *Improvement of Crop Plants for Industrial End Uses*, 209–251, copyrighted 2007 Springer)

Cellulose processing, primarily the manufacture of esters (viscose, nitrates, etc.), is preceded by a stage of its preliminary degradation in order to achieve the required average molecular mass and the optimum MMD. This is commonly done by hydrolysis or thermal treatment. Acidic or alkaline hydrolysis of cellulose makes it possible to achieve this goal. (Ershov, B. G., 1998).

Prevalent pretreatment methods:

The most commonly used methods for pretreatment of biomass are:

1. Chemical pretreatment

- a. Acid (Hydrochloric acid, Sulfuric acid, Perchloric acid
- b. Bases (Sodium Hydroxide, Calcium Hydroxide etc.)
- c. Ammonia gas
- d. Chlorine gas
- e. Oxygen gas

2. Physical treatment

- a. Mechanical crushing
- b. High temperature

3. Irradiation

- a. γ -ray treatment
- b. β -ray treatment
- c. α -particle treatment

4. Enzymatic treatment: The enzymes Cellulase and Cellobiase can also be used directly on the biomass for conversion of cellulose to simple sugars. The conversion in this case is not very high and requires a very high concentration of enzymes to be used.

Enzymes are very expensive and hence using enzymes directly doesn't justify the costs involved.

None of these treatments is effective alone and more often than not, pretreatments are done in combination to increase the overall yield. Mostly, the size of the biomass particle is reduced first through mechanical crushing. This helps in exposing the inner part of Lignocellulosic network. After this, chemical and high temperature treatment is given to biomass to increase its digestibility and convert cellulose to glucose or other smaller sugars.

Why do we need irradiation as a pretreatment: The chemical treatments are very effective in converting cellulose to glucose but there are some disadvantages associated with it. (Ershov, B. G., 1998) An average molecular mass and optimal Molecular Mass Distribution (MMD) is required before hydrolyzing the materials. Chemical hydrolysis can achieve this process but the process is laborious, time intensive, involves loss of materials and causes environmental damage.

Irradiation as a pretreatment: Use of penetrating radiations for treating biomass has been proved very effective in converting the complex carbohydrates into soluble sugars or to increase the conversion efficiency of other methods of treatments. (Ershov, B. G., Klimentov, A. S., 1984)

When cellulose is exposed to ionizing radiation, local explosions in the pyranose ring occurs which results in the breakage of intermolecular hydrogen bonds. On exposure to ionizing radiation, some of the "ejected" electrons are stabilized in intermolecular traps but because of the crystallinity present in cellulose, the concentration of these traps is insufficient and can not suppress the recombination of the "electron-hole" ion pairs, bound to Coulombic interaction. The excitations produced are localized and lead to rupture of C-H bonds at positions 1 and 4. Also, formation and accumulation of radicals and new functional groups takes place. New functional groups are formed at the points where rupture took place. These polar groups (e.g., carbonyl and carboxyl) affect the effective characteristic viscosity of the solution and act as acceptors of electrons and other excited states thus their accumulation results in a decrease in rate cellulose degradation. (Ershov, B. G., Klimentov, A. S., 1984; Rutherford, H.A., 1963)

Some of the gases released during irradiation of cellulose are hydrogen, carbon monoxide, carbon dioxide and methane. (Arthur J. C., Segal L., 1974) Analysis has shown that carbonyl and carboxyl groups are formed in irradiated cellulose. (Imamura, R., Ueno,

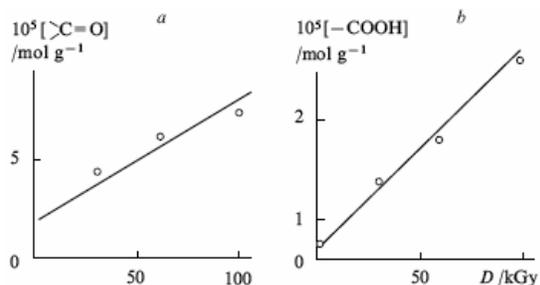


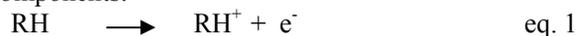
Figure 3: Dependence of the accumulation of carbonyl (a) and carboxy (b) groups in cellulose on the absorbed dose. (Adopted from Ershov, B. G., Klimentov, A. S., 1984)

T. & Murakami, K., 1972; Ershov, B. G., Klimentov, A. S., 1984)

The irradiated cellulose contains water soluble and water-insoluble fractions. Some of the compounds identified after hydrolysis of water soluble fraction of irradiated cellulose give xylose, arabinose, gluronic acid, formic acid and malonic dialdehyde. (Brenner, W. W., Rugg, B. A. & Rogers, C., 1977) No appreciable rupture of C-OH, C-C and C-O-C has been reported.

The radiation degradation of cellulose is accompanied by a decrease in the width of the molecular mass distribution, and with increase in the absorbed dose, a monodisperse distribution is approached. A decrease in the polydisperse character of technical celluloses at high absorbed doses (500—1000 kGrad) has been noted. (Simionescu, C., Butnaru, R. & Rozmarin, G., 1973) It has also been established that a change in the molecular mass distribution of cellulose takes place even at low doses. Thus the non-uniformity coefficient decreases from 1.3 for the original cellulose to ~0.4 for irradiated cellulose (for an absorbed dose of 3.2 kGrad). (Ershov, B. G., Klimentov, A. S., 1984)

Mechanism of radiation-chemical transformations of cellulose: The first step of action of an ionizing radiation on cellulose (RH) is ionization of its components:



Because of the Coulombic force between the excited electron and the positive atom causes the recombination of two leading to



A very low yield of stabilized electrons, 5% of the overall yield of radicals after γ irradiation at 70K, suggests that the recombination process predominates. This process is favored considerably by a crystal-like and rigid structure of the polymer. (Ershov, B. G., 1998) But the charge migration is completed at the defects of the crystal structure (mainly amorphous region) resulting in the formation of excited fragments

of the polymer These fragments decompose with preferential cleavage of the C(1)-H and C(4)-H bonds of the glucopyranose ring:



The hydrogen atoms take out another hydrogen atom from other carbon atoms at their corresponding positions:



The resulting R· radicals are unstable and decompose with the cleavage of the glucosidic bond to give radicals 1 and 2 and with scission of the glucopyranose ring. (Ershov B. G., 1998)

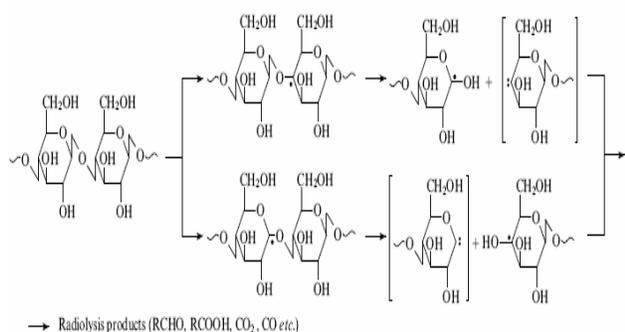


Figure 4: Mechanism of Radiation chemical transformation of Cellulose. (Adopted from Ershov, B. G. 1998)

Effect of Lignin: In nature, cellulose is often found in association with lignin. In situ irradiation of cellulose results in much lesser degradation than pure cellulose because of the protective action of lignin. The aromatic groups present in lignin are known to act as protectors when other organic compounds were irradiated in their presence. (Campbell, F. J., 1981) This may be due to the transfer of the excitation energy from the cellulose complex to lignin. Apart from radical 1 and 2 (discussed previously) a lignin type radical was also detected in the ESR spectrum while analyzing the quantitative and qualitative composition of radicals at 77 and 300 K. It was confirmed that this was a phenoxyl radical formed upon cleavage of the ether lignin ± carbohydrate bond. (Ershov B. G., 1998) A higher yield of cellulose radicals upon γ-irradiation at 77K was found for pure cellulose (2.7) than that for aspen wood (0.8). The yield of lignin radicals is 1.7. Thus, the efficiency of in situ degradation of cellulose changes noticeably over a wide temperature range in which the plant tissue is irradiated; this can be explained by the protective effect of lignin present in it. (Ershov B. G., 1998)

Radiation-thermal degradation of cellulose: Upon γ radiation-thermal degradation of cellulose, two

temperature ranges of the radiation-induced degradation of cellulose were found: <380 K, where the yields did not change much, and >380 K, where the yields increase markedly with temperature. The contribution of thermal degradation in the γ-irradiation was taken into account in the calculation of the yields, although it is insignificant. The activation energy was determined to be 23.4±1.6 kJ per mol (Heller, H., McConnell, H. M., 1960) which most probably corresponds to the diffusion of radicals in the polymer. Since activation energy corresponds to the energy of conformational vibrations of the gluco-pyranose ring, an increase in temperature initiates the transfer of the radical state to the nearest polymeric chain and causes its degradation. (Golova, O.P., 1975) Radiation-induced degradation at high temperatures is accompanied by the formation of hydrogen and carbon dioxide. The yield of the latter is about two times higher. These facts indicate that the radiation-induced degradation of cellulose at temperatures above 380 K occurs by a chain mechanism, which is initiated by radicals formed upon irradiation. (Fig. 5) (Ershov, B. G., 1998)

T/K	G _d	G _{CHO}	G _{COOH}
303	5.1	5.4	1.8
363	6.0	5.8	1.8
393	7.4	7.1	1.8
413	10.7	11.1	1.9
423	11.4	–	–
433	16.8	17.1	2.3
443	18.1	–	–
463	27.7	26.0	3.3

Figure 5: Yields of products upon thermal degradation of cellulose. (Adopted from Ershov, B. G., 1998)

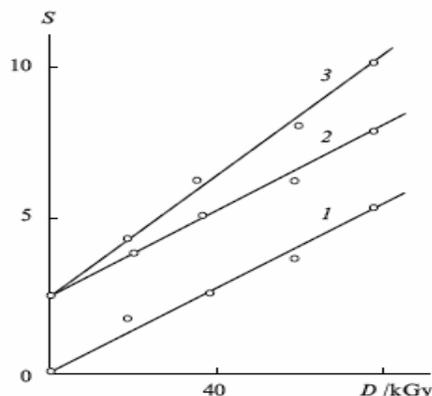


Figure 6: Dependence of number of bond scissions (S) in wood cellulose on the absorbed dose, (1) radiation treatment, (2) successive thermal and radiation treatment, (3) successive radiation and thermal treatment. Thermal treatment was carried out at 463K for 3 hrs. to achieve steady state and radicals in cellulose upon irradiation which activate scission on heating. (Adopted from Ershov, B. G., 1998)

Degradation of cellulose upon sequential irradiation and thermal treatment: The order of irradiation and thermal treatment affects the degradation of cellulose to a large extent. (Ershov B. G., 1998) After irradiation or thermal treatment, the degree of polymerization of cellulose decreases, while the amount of reducing sugar obtained on its acid hydrolysis increases. When we heat the sample first and then irradiate, the increase in the amount of reducing sugar is approximately the sum of the increments corresponding to each of the effects but when heating is done after irradiation, a large increase in the amount of reducing sugar was observed. Figure 6 (Ershov B. G., 1998)

The higher yield in the irradiation and then heating method might be due to the formation of defects such as weakened bonds, reactive groups

Literature review of the treatments given and results obtained so far:

1. (Kumakura, M., Kaetsu, I., 1978) compared the yield of reducing sugar for mechanically crushed and mechanically crushed and e-beam irradiated (in air) samples of rice straw, chaff and saw dust. They found that there is a very small increase in the yield of reducing sugars by increasing the extent of mechanical damage done to the sample but a large increase (~ 5 times) was noticed when the sample were irradiated with different doses of e-beam after mechanical treatment. (Figure 7, 8) A comparison of % sugar yield based on the effectiveness of mechanical treatment is done in figure 9. It shows that at low doses, mechanical pretreatment is very effective but at higher doses the effect of mechanical treatment is not so significant.

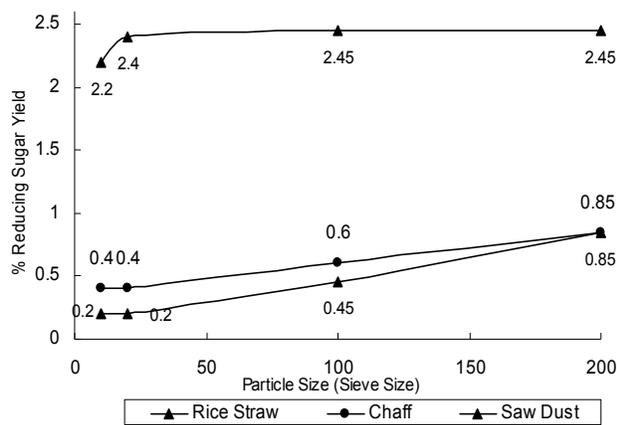


Figure 7: Reducing Sugar Yield on Mechanical Pretreatment of Biomass. (Kumakura, M., Kaetsu, I., 1978)

2. When the above samples were hydrolyzed using Cellulase enzyme, a large increase in yield was reported. The yield increases up to a value of 80 when the irradiated samples were hydrolyzed for

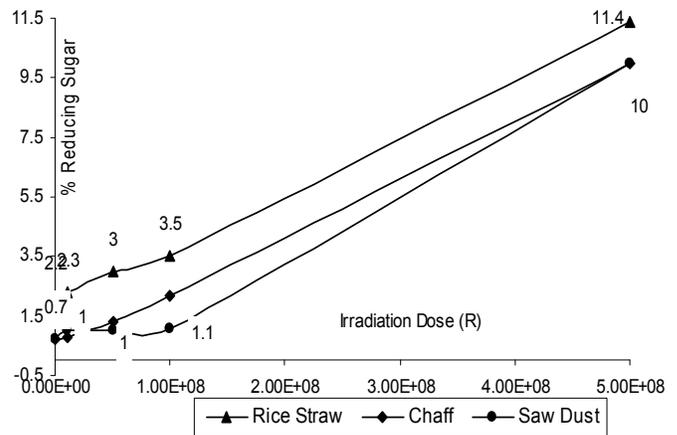


Figure 8: Reducing Sugar Yield on e-Beam Pretreatment of Biomass after Mechanical Treatment (Kumakura, M., Kaetsu, I., 1978)

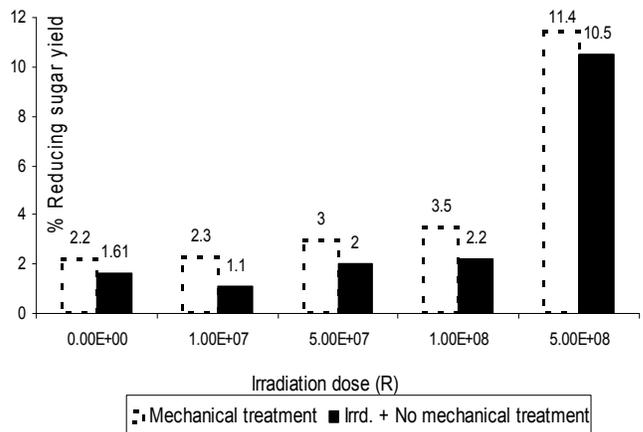


Figure 9: Comparison in reducing sugar yield with and without mechanical treatment for Rice straw. (Kumakura, M., Kaetsu, I., 1978)

35 hrs. Shown in figure 10 are the results for rice straw.

- (Kumakura, M., Kaetsu, I., 1984) performed an experiment this time putting acid treatment after e-beam and then hydrolyzing the samples by Cellulase. They compared the % glucose yields for sulfuric acid after no irradiation and after a dose of 2×10^7 R for differential time and temperature. % glucose yield can be defined as the wt. of glucose formed per weight of dry sample taken. They found out that time of hydrolysis can be significantly decreased for same or higher yields if higher temperatures are used. Figure 11
- (Kumakura, M., Kaetsu, I., 1984) also compared the yields of reducing sugars formed after an acid treatment by HCl following two different doses of irradiation by e-beam. Confusion here is that in the same research work, they have calculated yields in

two different ways for treatment by two different acids. Hence, the results can not be compared. Figure 12.

Hydrolysis time (hr.)	0 R	10 ⁷ R	5* 10 ⁷ R	10 ⁸ R	5* 10 ⁸ R
6	9	12	17	24	38
10	14	19	26	35	54
24	28	33	40	53	82
35	30	35	48	59	80

Figure 10: Showing increase in reducing sugar yield with increase in radiation dose and hydrolysis time with Cellulase. (Kumakura, M., Kaetsu, I., 1978)

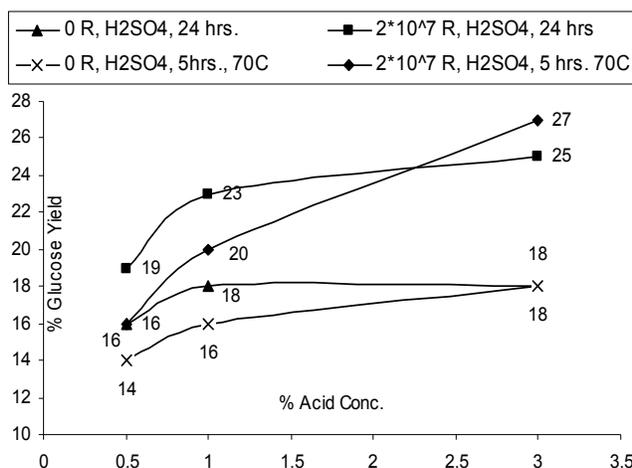


Figure 11: % Glucose yield after treatment with e-beam + acid hydrolysis + enzyme hydrolysis of chaff. (Kumakura, M., Kaetsu, I., 1984)

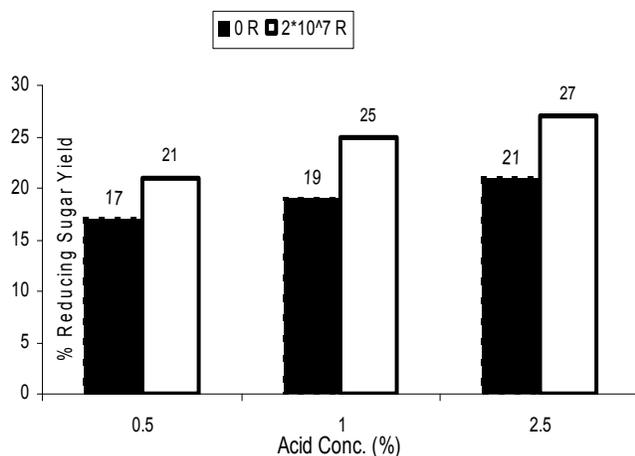


Figure 12: % Reducing Sugar Yield After Treatment With e-Beam + HCl for 24 Hrs. on Chaff. (Kumakura, M., Kaetsu, I., 1984)

5. (Lu, Z. X., 1993) used NaOH as a chemical pretreatment agent after e-beam pretreatment to find out the percent glucose yield. or a constant alkali conc. of 4% and a hydrolysis time of 24 hrs, approximate 50% increase in glucose yield was found when the irradiation dose was increased from 10⁷ to 10⁸. Figure 13.

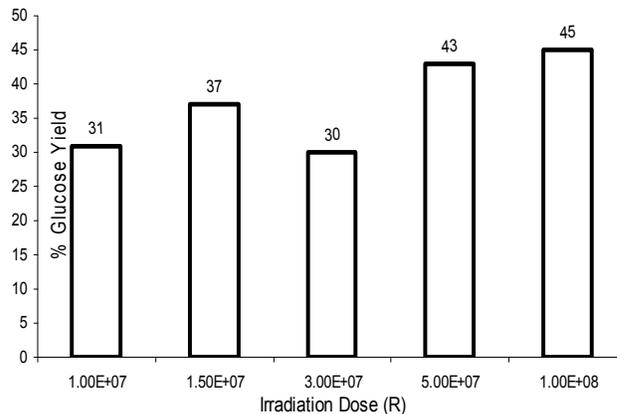


Figure 13: % Glucose Yield After Treatment With e-Beam + NaOH (4%) + Enzyme on Chaff. (Lu, Z. X., 1993)

Discussion: Biofuels are a great source of energy. They help reduce the burden on conventional energy resources. Development of biofuels will also help in keeping the food products in the food chain instead of putting those for the production of ethanol (eg. Corn). Bioethanol is better than biodiesel in a sense that we don't need to do separate cultivation of crops to produce bioethanol as is the case for the production of biodiesel (eg. Jatropha). The biomass is a natural product left after we use the crops and can still be utilized based on its high lignocellulose content.

Also, usage of biomass as a source of biofuel will help in reducing the problem of waste dumping since the waste is being utilized for energy generation.

One of the draw backs currently associated with this technology is that its very energy intensive. The amount of energy consumed to irradiate the material to cause desirable changes is humongous and makes the process economically unviable.

In the future, we require to research more on how this treatment can be made effective at low doses of irradiation.

Conclusion: Irradiation of biomass can be an important technology in the future. This can serve as a pretreatment step in conjugation with other pretreatment technologies to facile the conversion of cellulose to fermentable sugar. Irradiation using different high energy sources leads to structural

breakdown of the material. It results in loss of viscosity, structural strength and generation of several small chemicals including fermentable sugars.

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