IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)

An International Open Access, Peer-reviewed, Refereed Journal

ETHANOL PRODUCTION, PURIFICATION, AND ANALYSIS TECHNIQUES

Laxman S. Nimangre*, Pranali P. Patil , Poournima S. Sankpal,

Dr. Sachinkumar V. Patil,

Ashokrao Mane College of pharmacy, Peth-Vadgaon, Kolhapur, Maharashtra, India. (416112)

Affiliated to Shivaji university, Kolhapur, Maharashtra.

➢ Abstract:

World ethanol production rise to nearly 13.5 billion gallon in 2006. Ethanol has been part of alcoholic beverages for long time, but its application has expanded much beyond that during the 20th Century. Much of the recent interest is in the use of ethanol as fuel. In this paper, we have reviewed published literature on current ethanol production and separation methods, and chemical and sensory analysis techniques. Ethanol produced by fermentation, called bioethanol, accounts for approximately 95% of the ethanol production. It is recently widely used as an additive to gasoline. Corn in the Unites States and sugarcane in Brazil are widely used as raw materials to produce bioethanol. Cellulosic materials are expected to be the ultimate major source of ethanol and also represent a value-adding technology for agricultural coproducts. While bioethanol is considered as a sustainable energy source, it requires further purification for uses other than fuel. The most common purification technique utilized in the ethanol industry is rectification by further distillation. However, distillation has critical disadvantages including high cost and limited separation capacity. Several alternatives have been proposed to replace distillation such as non-heating fractional distillation by ultrasonic irradiation, oxidation of impurities by ozone, and adsorption of impurities by activated carbon or zeolite. Chemical and sensory analyses are used to determine the quality of alcohol and to optimize various steps in production. Near-infrared (NIR) spectrometry, high performance liquid chromatography (HPLC), gas chromatography (GC), and mass spectrometry (MS), have been developed for chemical analyses. Also, olfactometry is common for sensory analysis. This paper summarizes the state-of-the art of ethanol production, purification, and analytical techniques.

➢ Keywords:

Activated carbon, chemical analysis, ethanol, ozone, production process, purification, renewable fuels, substrates.

1. Introduction

World ethanol production rise to nearly 13.5 billion gallon in 2006. Today, various kinds of crops are utilized for ethanol production. In the United States, the world biggest ethanol producer, ethanol is mainly produced corn. Brazil, the second biggest ethanol producer, utilizes sugarcane as the ethanol substrate. European countries produce ethanol from beet. Also, intensive studies are going on ethanol production from lignocellulosic biomass. Ethanol production from lignocellulosic biomass could find a way to utilize agricultural waste for ethanol production.

Ethanol purification is critical for any kind of purpose. In the industry, purification is done by mainly distillation. Although distillation is a strong separation technique, it has several disadvantages, mainly its separation capacity of volatile compounds and cost. Not many studies have done on the area of ethanol purification techniques which could take a place of distillation.

However, it is expected that purification techniques for water and wastewater, such as ozonation, adsorption, and gas stripping, are applicable to ethanol.

Ethanol analysis techniques have been developed to improve the value of ethanol. Gas chromatography (GC) and High performance liquid chromatography (HPLC) are common techniques to identify and quantify components of ethanol. Infrared spectroscopy (IR) is used for quality assurance of ethanol. Olfactometry coupled with GC enhances the flavour analysis of alcoholic beverages.

With a rapid increase in ethanol production, more extensive researches on ethanol have done recently. In this paper, the current ethanol production, purification, and analysis techniques are reviewed. The comprehensive knowledge of the current ethanol study will encourage further studies on ethanol

2. Ethanol production

2.1 Substrates

Ethanol is produced from various kinds of substrates. The substrate used for ethanol production is chosen based on the regional availability and economical efficiency. In this section, the substrate for ethanol fermentation is discussed.

2.1.1 Sucrose containing materials

Ethanol is produced by fermentation. Fermentation process is a process to convert sugar to ethanol. Sucrose containing materials could simplify the ethanol production process.

• Sugarcane

Brazil is the world second biggest ethanol producer. In Brazil, sugarcane is the major substrate for ethanol (1). Countries in Central America and Caribbean are suitable for sugarcane cultivation, and their ethanol production is increasing recently.

• Sugar beet

Sugar beet is mainly cultivated in European countries (2) since it grows under cold climate.

• Sugar sorghum

Sugar sorghum is also a sucrose containing crop. It yields large amount of biomass and sugar due to its high photosynthetic efficiency (3).

2.1.2 Starchy materials

Starch is converted to sugar by saccharification followed by fermentation. Today, saccharification and fermentation are done simultaneously (SSF: simultaneous saccharification and fermentation).

• Corn

It is relatively easy to obtain high purity starch from corn. As the world biggest corn producer, the United States mainly produces ethanol from corn, and this also makes the United States the world biggest ethanol producer.

• Other starchy materials

Any kind of starch containing crop can be used to produce ethanol. Many researches on ethanol production from various starchy materials, such as potato (4), sweet potato (5), cassava (6), and wheat (7), have been investigated.

2.1.3 Lignocellulosic biomass

Many studies are going on for ethanol production from lignocellulosic biomass. Lignocellulosic materials include maize silage (8), barely hull, and paper sludge (9). The difficulties of using lignocellulosic materials are there poor porosity, high crystallinity, and lignin contents. Various kinds of pre-treatment techniques have been investigated, such as steam (10), acid (11), and alkali (12) treatments.

2.2 Production process

Starchy materials are converted to ethanol by two major processes, dry milling and wet milling.

2.2.1 Dry milling

Dry milling the dominant and more efficient ethanol production process than wet milling. It produces about 2.8 gallons of ethanol per bushel of corn (13). The a schematic of dry milling is shown below (Figure 1).

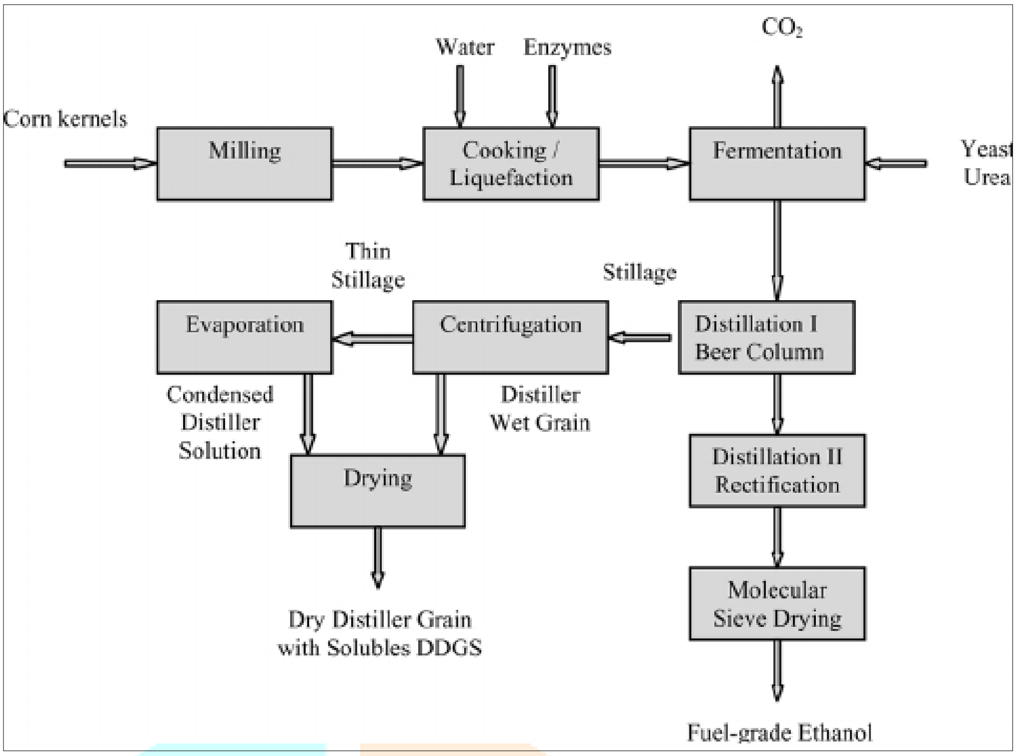

Figure 1. Schematic of dry milling ethanol production (14)

2.2.2 Wet milling

The components of grain are separated in wet milling before saccharification. Produces various high value products such as corn gluten meal (CGM) and corn gluten feed (CGF) are produced though wet milling. It produces about 2.7 gallons of ethanol per bushel of corn (13). The schematic of wet milling is shown below (Figure 2).

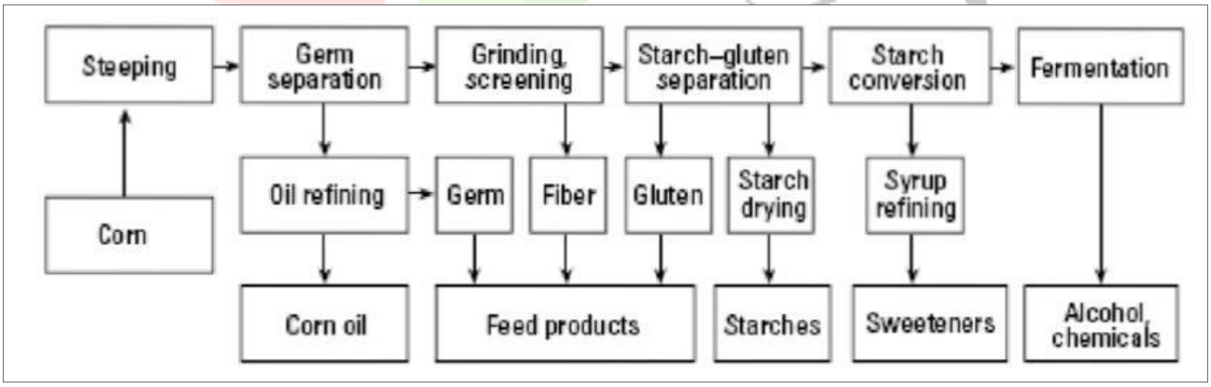

Figure 2. Schematic of wet milling ethanol production (15)

3. Ethanol purification

3.1 Fermentation by-products

Ethanol is produced by yeast fermentation. Although yeast mainly produces ethanol, it also produces by-products. These by-products need to be removed to obtain pure ethanol. There are mainly two kinds of by-product sources, starch and lignin. Starch derived by-products include esters, organic acids, and higher alcohols. Lignin derived by-products include cyclic and heterocyclic compounds.

3.2 Purification techniques

Fermentation by-products are mostly removed by distillation. However, volatile by-products tend to lodge more in ethanol. Also, especially for drinking or pharmaceutical purpose, high concentration of ethanol is not required. In this case, further distillation is just waste of energy and money. Many studies have done to find a new purification technique of ethanol which can take place of distillation.

3.2.1 Distillation

Distillation is the most dominant and recognized industrial purification technique of ethanol. It utilizes the differences of volatilities of components in a mixture. The basic principle is that by heating a mixture, low boiling point components are concentrated in the vapour phase. By condensing this vapour, more concentrated less volatile compounds is obtained in liquid phase.

Distillation is one of the most efficient separation techniques. However, it contains several problems. One is separation of volatile compounds. In ethanol production, a distillation tower is designed to separate water and ethanol effectively. Water is obtained from the bottom of the tower and ethanol is obtained from the top of the tower. It is expected that impurities with similar boiling points to ethanol lodges in even after distillation. Second is its cost. Distillation is a repetition of vaporization and condensation. Therefore, it costs a lot.

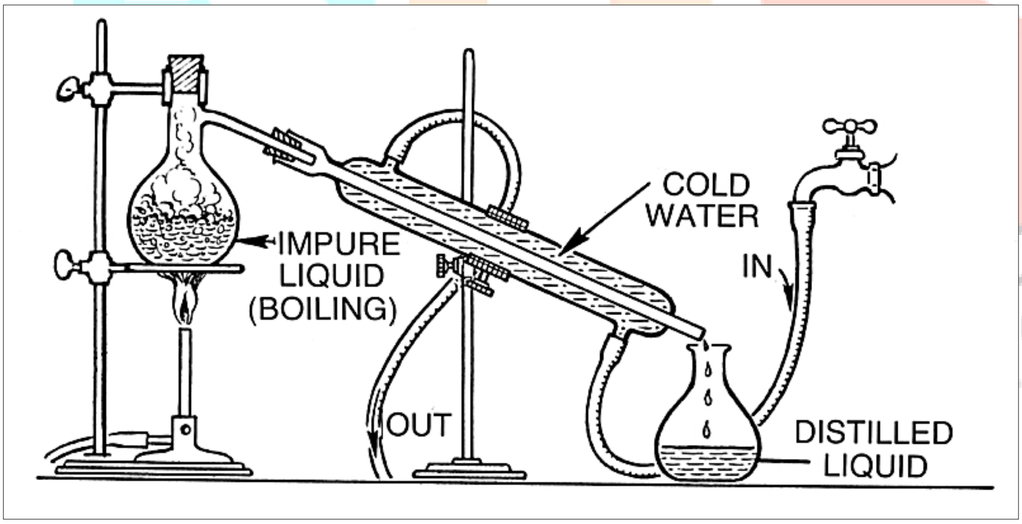

Figure 3.Purification of ethanol by distillation

3.2.2 Adsorption

Adsorption is a separation technique utilizing a large surface area of adsorbent. Compounds are simply adsorbed on the adsorbent depending on their physical and chemical properties. In general, bigger particles tend to be adsorbed more due to their low diffusivities. Also, compounds with the similar polarity to the adsorbent surface tend to be adsorbed more. When purification of ethanol is considered, non-polar surface and wide ranging pore distribution are favorable since ethanol is polar compounds and various sizes of particles could be contained in ethanol as impurities. From water treatment, activated carbon) (16) and activated alumina (17) are the most expectable adsorbents.

3.2.3 Ozonation

Ozone is a tri-atomic molecule consisted by three oxygen atoms. Ozone could decompose various kinds of compounds using its strong oxidation potential. Decomposition of compounds could result in changes in physical and chemical properties of compounds such as increases in volatility, biodegradability, and a decrease in toxicity. Although oxidation of ethanol could be expected with oxidation, it does not happen under the atmospheric condition (18).

Thus, ozone can remove impurities without a significant damage on ethanol. There are still some problems, non-oxidizable compounds and ozonolysis by-products. It is expected that some compounds cannot be oxidized by ozone. These compounds will remain after ozonation.

Also, ozonation is an oxidation process and not remove compounds physically. Thus, ozonation could generate new compounds, ozonolysis by-products. These compounds should be removed after ozonation by post-ozonation treatments.

3.2.4. Gas stripping

Gas stripping is a separation technique utilizing the differences of volatilities among compounds. The separation efficiency is simply governed by Henry's law constant (Alley, 2007).

$H = P_{vap} / C_{sat}$

Where H = Henry's constant (moles/L atm)

Pvap = the partial pressure of a pure compound (atm), and

Csat = the saturation concentration of the pure compound in the liquid phase (mols/ or mg/L)

Henry's law constant varies depending on the vapor and liquid phases. It is easily imagined that compounds with low boiling points can be stripped more easily such as acetaldehyde which is one of the major impurities in ethanol.

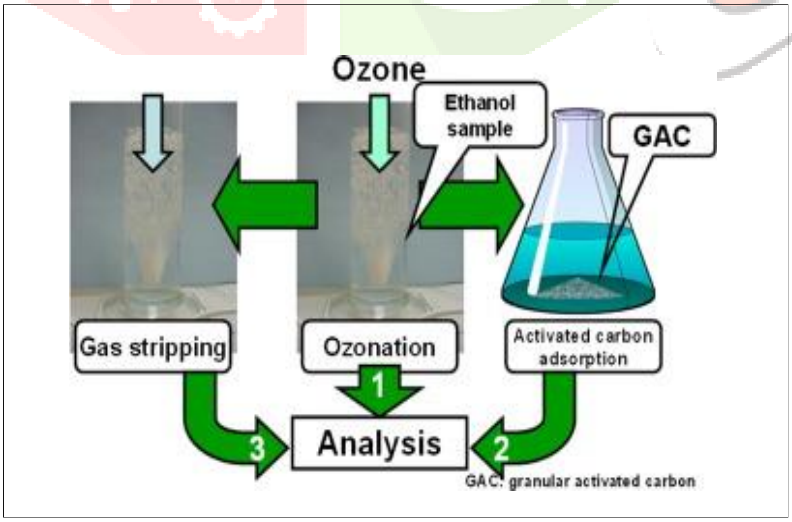

Figure 4.Purification of ethanol by ozonation

4. Ethanol analysis

4.1 Gas chromatography

Gas chromatography (GC) is an analytical technique for volatile and semi-volatile compounds. Many ethanol analyses have done with GC since impurities in ethanol are basically volatile as well as ethanol itself (19,20,21). A sample is vaporized at an injection port by heat. The sample vapour is sent to column packed with adsorbent or absorbent. Inside column, each component in sample is separated depending on its physical and chemical property. The end of column the concentration of each compounds are measured by a detector. There are many kinds of coatings for column. A coating should be chosen depending on the target compounds. Also, there are many kinds of detectors. Each detector has advantages and disadvantages. Thus, a detector should also be chosen carefully to detect target compounds. Gas chromatography-mass spectrometry (GC-MS) is an integrated system of two analytical equipments. Gas chromatography separates analytes and mass spectrometry identifies them. GC-MS accelerates ethanol analysis with its simultaneous separation and identification capavities. A typical GC chromatogram of alcoholic beverage is shown in

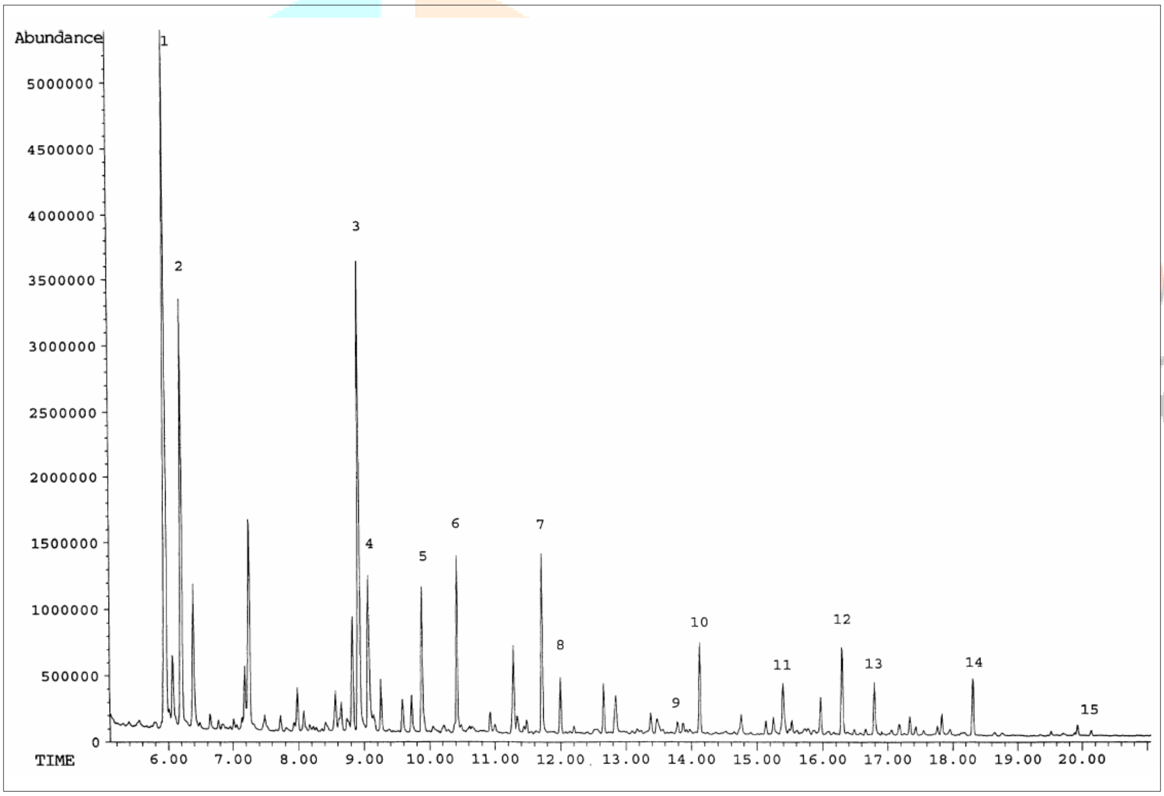

figure 5. Figure 5. Typical GC chromatogram of alcoholic beverage (rum) (22)

4.2 High performance liquid chromatography

High performance liquid chromatography (HPLC) is an analytical technique which utilized liquid as the mobile phase instead of gas of GC. Samples are not heated at the injection port. Thus, non-volatile compounds or heat sensitive compounds can be analyzed with HPLC.

Many extensive researches for ethanol analysis with HPLC have done (23,24,25). A typical HPLC chromatogram of alcoholic beverage is shown in figure 6. While HPLC is more comprehensive than GC in terms of sample limitation, it is still expensive and less sensitive comparing to GC

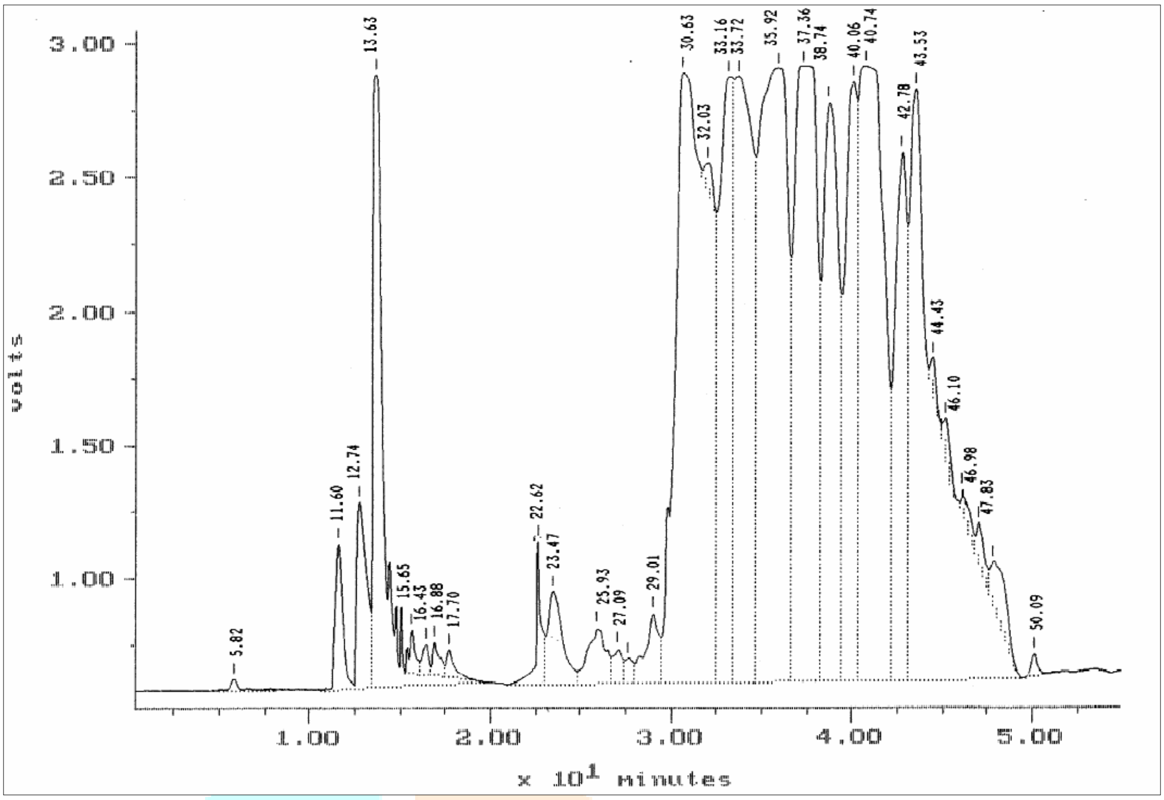

Figure 6. Typical HPLC chromatogram of alcoholic beverage (wine)

4.3 Infrared spectroscopy

Infrared spectroscopy (IR) is an analytical technique utilizing infrared adsorption. Infrared with different wavelengths are passed though a liquid sample. Infrared is adsorbed by a compound, and the absorbability of infrared varies among different compounds and different infrared wavelengths. Samples are identified by comparing absorbability of infrared,. IR does not have as high resolution as GC or HPLC. However, the equipment is relatively cheap and analysis is simple and quick. Thus, it utilizes more for quality assurance (26) and classification purposes (27). A typical IR sectraa of alcoholic beverage is shown in figure 7.

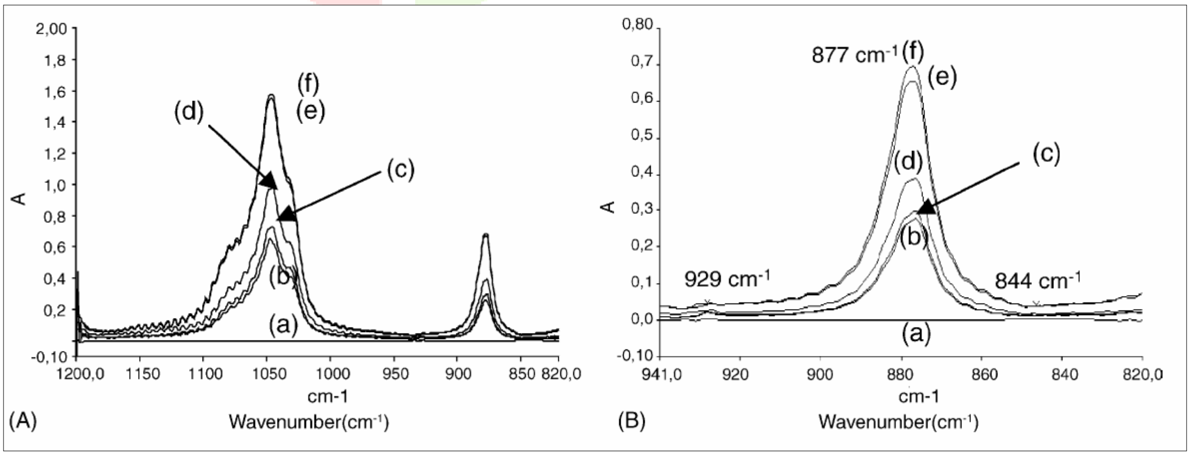

Figure 7. Typical FTIR spectra of different commercial alcoholic beverages

4.4 Olfactometry

Olfactometry is a sensory analysis usually coupled with GC. For a typical GC-Olfactometry (GCO) system, a GC column is connected to a separator where analytes are separated to two ways, olfactometry and a detector such as FID, PID, and MS. Olfactometry is a simple system which is just an open-end column, and a panelist sniffs analytes coming from the column. The panelist records the odour character and intensity of the analyte which correspond with a peak in chromatogram. Olfactometry provides flavours data rather than stoichiometric chemical data. It is utilized for alcoholic beverage analysis to develop its flavour.

5. Conclusion

In this paper, the current ethanol production, purification, and analysis techniques have been reviewed. Ethanol is produced from various kinds of substrates. The substrates used for ethanol production vary by different countries due to their different farming conditions. In the United States, corn is the dominant substrate of ethanol, and in Brazil, sugarcane is used for ethanol production. Also, from the environmental stand point, utilization of lignocellulosic biomass for ethanol production is being studied more intentionally. Ethanol is purified almost only by distillation in the industry.

Although distillation is one of the most effective liquid-liquid separation techniques, it contains some critical disadvantage, cost and limitation on separation of volatile organic compounds. Many purification techniques of water and wastewater are expected to be applied to ethanol purification as well. Ozonation could degrade impurities. Activated carbon could remove impurities without adsorbing ethanol, and gas stripping could simply remove high volatile compounds without any heating. Ethanol analysis is done with different kinds of analytical techniques. While, currently, GC has advantages on the resolution of analysis, HPLC could be used for heat sensitive analytes. IR is convenient for routine quality assurance or classification of ethanol. Also, olfactometry is utilized for flavour analysis of alcoholic beverages.

6. References

1. Goldemberg, J., S. T. Coelgo, and P. Guardabassi. 2008. The sustainability of ethanolnext term production from previous termsugarcane. Energy policy. 36(6): 2086-2097.
2. Power, N., J. D. Murphy, E. McKeogh. 2008. What frop rotation will provide optimal firstgeneration ethanol production in Ireland, from technical and economical perspective Energy. 33: 385-399.
3. Giorgis, F., C. F. Tresso, P. Rava, A. M. Paterson, G. R. Doqling, D. A. Chamberlain, E. Billa, D. P. Koullas, B. Monties, E. G. Koukios. 1997. Structure and composition of sweet sorghum stalk components. Industrial Crops and Products. 6: 297-302.
4. Quintero, J. A., M. I., Montoya, O. J. Sanchez, O. H. Giraldo, and C. A. Cardona. 2008. Fuel ethanol production from sugarcave and corn: Comparative analysis for Colombian case. Process Biochemistry. 34: 115-119.
5. Sree, N. K., M. Sridhar, L. V. Rao, and A. Pandey. 1999. Ethanol production in solid substrate fermentation using thermotolerant yeast. Process Biochemistry. 34: 115-119.
6. Tripathy, S. S. and A. M. Raichur. 2008. Enhanced adsorption capacity of activated alumina by impregnation with alum for removal of As(V) from water. Chemical Engineering Journal. 138: 179-186.
7. Leng, R., C. Wang, C. Zhang, D. Dai, and G. Pu. 2008. Life cycle inventory and energy analysis of cassava-based Fuel ethanol in China. Journal of Cleaner Production. 16: 374-378.
8. Murphy, J. D., and N. M. Power. 2008. How can we improve the energy balance of ethanol production from wheat? Fuel. 87: 1799-1806.
9. Oleskowicz-Popiel, P., P. Lisiecki, J. B. Holm-Nielsen, A. B. Thomsen, and M. H. Thomsen. 2008. Ethanol production from maize silage as lignocellulosic biomass in anaerobically digested and wet-oxidized manure. Bioresource Technology. 99(13): 5327-5334.
10. Marques, S., L. Alves, J. C. Roseiro, F. M. Gírio. 2008. Conversion of recycled paper sludge to ethanol by SHF and SSF using Pichia stipitis. Biomass and Bioenergy. 32(5): 400-406.
11. Linde, M., E.-L. Jakobsson, M. Galbe, and G. Zacchi. 2008. Steam pretreatment of dilute H2SO4-impregnated wheat straw and SSF with low yeast and enzyme loadings for bioethanol production. Biomass and Bioenergy. 32(4): 326-332.
12. Nichols, N. N., L. N. Sharma, R. A. Mowery, C. K. Chambliss, G. P. van Walsum, B. S. Dien, and L. B. Iten. 2008. Fungal metabolism of fermentation inhibitors present in corn stover dilute acid hydrolysate. Enzyme and Microbial Technology. 42(7): 624-630.
13. Hu, Z., Z. Wen. 2008. Enhancing enzymatic digestibility of switchgrass by microwave-assisted alkali pretreatment. Biochemical Engineering Journal. 38(3): 369-378.
14. Rendleman, C. M., H. Shapuri. 2007. New Technologies in Ethanol Production: USDA Agricultural Economic Report Number 842. Available at: www.nass.usda.gov. Accessed 23 April 2008.
15. Kim, Y., N. Mosier, M. R. Ladisch. 2008. Process simulation of modified dry grind ethanol plant with recycle of pretreated and enzymatically hydrolyzed distillers' grains. Bioresource Technology. 99(12): 5177-5192.

16. Saunders, D. S., F. I. Meredith, and K. A. Voss. 2001. Control od Fumonisin: Effects of Processing. Environmental Health Perspectives. 109: 333-336.
17. Demirbas, E., M. Kobya, and M. T. Sulak. 2008. Adsorption kinetics of a basic dye from aqueous solutions onto apricot stone activated carbon. Bioresource Technology. 99(13): 5368-5373.
18. Tripathy, S. S. and A. M. Raichur. 2008. Enhanced adsorption capacity of activated alumina by impregnation with alum for removal of As(V) from water. *Chemical Engineering Journal*. 138: 179-186.
19. Bailey, P. S. 1982. Ozonation in organic chemistry. New York, N.Y.: Academic press, Inc.
20. Hida, Y., K. Kudo, N. Nishida, and N. Ikeda. 2001. Identification of reddish alcoholic beverages by GC/MS using aroma components as indicators. Legal Medicine. 2(4): 237-240.
21. Campo, E., J. Cacho, and V. Ferreira. 2007. Solid phase extraction, multidimensional gas chromatography mass spectrometry determination of four novel aroma powerful ethyl esters: Assessment of their occurrence and importance in wine and other alcoholic beverages. Journal of Chromatography A. 1140: 180-188.
22. Rodrigues, F., M. Caldeira, and J.S. Câmara. 2008. Development of a dynamic headspace solid-phase microextraction procedure coupled to GC–qMSD for evaluation the chemical profile in alcoholic beverages. Analytica Chimica Acta. 609(1): 82-104.
23. Garruti, D. S., M. R. B. Franco, M. A. A. P. da Silva, N. S. Janzantti, and G. L. Alves. 2006. Assessment of aroma impact compounds in a cashew apple-based alcoholic beverage by GC-MS and GC-olfactometry. LWT - Food Science and Technology. 39(4): 373-378.
24. Sen, N. P., S. W. Seaman, B. P. -Y. Lau, D. Weber, and D. Lewis. 1995. Determination and occurrence of various tetrahydro-β-carboline-3-carboxylic acids and the corresponding N-nitroso compounds in foods and alcoholic beverages. Food Chemistry. 54(3): 327-337.
25. Yarita, T., R. Nakajima, S. Otsuka, T. Ihara, A. Takatsu, and M. Shibukawa. 2002. Determination of ethanol in alcoholic beverages by high-performance liquid
26. chromatography–flame ionization detection using pure water as mobile phase. Journal of Chromatography A. 976: 387-391.
27. Alcázar, A., J. M. Jurado, F. Pablos, A. G. González, and M. J. Martín. 2006. HPLC determination of 2-furaldehyde and 5-hydroxymethyl-2-furaldehyde in alcoholic beverages. Microchemical Journal. 82(1): 22-28.
28. Lachenmeier, D. W. 2007. Rapid quality control of spirit drinks and beer using multivariate data analysis of Fourier transform infrared spectra. Food Chemistry. 101(2): 825-832.
29. Pontes, M. J. C., S. R. B. Santos, M. C. U. Araújo, L. F. Almeida, R. A. C. Lima, E. N. Gaião, and U. T. C. P. Souto. 2006. Classification of distilled alcoholic beverages and verification of adulteration by near infrared spectrometry. Food Research International. 39(2): 182-189.