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COURSE: CHEMISTRY

MATRIC NO: 19/02/040

SOLUTION TO ASSIGNMENT

1) Classification of Alkanols

Alkanols can be classified as primary, secondary or tertiary depending on the location of the OH (hydroxyl or hydroxy) functional group. Chemists use o notation to refer to primary, secondary and tertiary alkanols:

primary alkanol ≡ 1o alkanol -OH on a terminal (end of chain) C atom secondary alkanol ≡ 2o alkanol -OH on a C atom bonded to 2 C atoms tertiary alkanol ≡ 3o alkanol -OH on a C atom bonded to 3 C atoms

The general structure of primary, secondary and tertiary alkanols is summarized in the table below: (Note that R, R', R" represent alkyl, CnH2n+1, chains)

Classification (o) General Formula Location of -OH group

Primary 1o

H | R- C -OH | H

-OH, on a terminal (end) carbon atom

Secondary 2o

H | R- C -OH | R'

-OH, on a carbon atom is bonded to 2 other carbon atoms

Tertiary 3o

R" | R- C -OH | R'

-OH, on a carbon atom is bonded to 3 other carbon atoms

2) 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 (Goldemberg et al., 2008). 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 (Power et al., 2008) since it grows under

cold climate.

• Sugar sorghum

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Sugar sorghum is also a sucrose containing crop. It yields large amount of biomass and sugar

due to its high photosynthetic efficiency (Giorgis et al, 1997).

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 (Quintero et al., 2008), sweet potato

(Sree et al., 1999), cassava (Leng et al., 2008), and wheat (Murphy and Power, 2008), have

been investigated.

2.1.3 Lignocellulosic biomass

Many studies are going on for ethanol production from lignocellulosic biomass. Lignocellulosic

materials include maize silage (Oleskowicz-Popiel et al., 2008), barely hull (Kim et al., 2008),

and paper sludge (Marques et al., 2008). The difficulties of using lignocellulosic materials are

there poor porosity, high crystallinity, and lignin contents. Various kinds of pretreatment

techniques have been investigated, such as steam (Linde et al., 2008), acid (Nichols et al.,

2008), and alkali (Hu and Wen, 2008) 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 (Rendleman and Shapouri, 2007). The

schematic of dry milling is shown below (Figure 1).

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Figure 1. Schematic of dry milling ethanol production (Kim et al., 2008)

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 (Rendleman and

Shapouri, 2007). The schematic of wet milling is shown below (Figure 2).

Figure 2. Schematic of wet milling ethanol production (Saunders et al., 2001)

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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 vapor phase. By

condensing this vapor, 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 ethanol even after distillation. Second is its cost. Distillation is

a repetition of vaporization and condensation. Therefore, it costs a lot.

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 (Demirbas et al., 2008) and

activated alumina (Tripathy and Raichur, 2008) 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 (Bailey, 1982).

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

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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).

sat

vap

C

P

H =

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.

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 (Hide et al., 2001, Campo et al., 2007, Rodrigues et al., 2008). A sample is

vaporized at an injection port by heat. The sample vapor 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 3.

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Figure 3. Typical GC chromatogram of alcoholic beverage (rum) (Garruti et al., 2006)

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 (Sen et al., 1995, Yarita et al.,

2002, Alcázar et al., 2006). A typical HPLC chromatogram of alcoholic beverage is shown in

figure 4. While HPLC is more comprehensive than GC in terms of sample limitation, it is still

expensive and less sensitive comparing to GC.

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Figure 4. Typical HPLC chromatogram of alcoholic beverage (wine) (Ferreira et al., 1999)

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 (Lachenmeier, 2007) and

classification purposes (Pontes et al., 2006). A typical IR sectraa of alcoholic beverage is shown

in figure 5.

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Figure 5. Typical FTIR spectra of different commercial alcoholic beverages (Gallignani et al.,

2005)

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 odor character and intensity of the analyte which correspond with a peak in

chromatogram. Olfactometry provides flavors data rather than stoichiometric chemical data. It is

utilized for alcoholic beverage analysis to develop its flavor.

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 flavor analysis of alcoholic beverages.

3) Reduction of Aldehydes and Ketones

The most common sources of the hydride Nucleophile are lithium aluminum hydride (LiAlH4) and sodium borohydride (NaBH4). Note! The hydride anion is not present during this reaction; rather, these reagents serve as a source of hydride due to the presence of a polar metal-hydrogen bond. Because aluminum is less electronegative than boron, the Al-H bond in LiAlH4 is more polar, thereby, making LiAlH4 a stronger reducing agent.

Addition of a hydride anion (H:-) to an aldehyde or ketone gives an alkoxide anion, which on protonation yields the corresponding alcohol. Aldehydes produce 1º-alcohols and ketones produce 2º-alcohols.

In metal hydrides reductions the resulting alkoxide salts are insoluble and need to be hydrolyzed (with care) before the alcohol product can be isolated. In the sodium borohydride reduction the methanol solvent system achieves this hydrolysis automatically. In the lithium aluminum hydride reduction water is usually added in a second step. The lithium, sodium, boron and aluminum end up as soluble inorganic salts at the end of either reaction. Note! LiAlH4 and NaBH4 are both capable of reducing aldehydes and ketones to the corresponding alcohol.

EXAMPLE 17.4.1

Mechanism

This mechanism is for a LiAlH4 reduction. The mechanism for a NaBH4 reduction is the same except methanol is the proton source used in the second step.

1) Nucleopilic attack by the hydride anion

2) The alkoxide is protonated

Biological Reduction

Addition to a carbonyl by a semi-anionic hydride, such as NaBH4, results in conversion of the carbonyl compound to an alcohol. The hydride from the BH4- anion acts as a nucleophile, adding H- to the carbonyl carbon. A proton source can then protonate the oxygen of the resulting alkoxide ion, forming an alcohol.

Formally, that process is referred to as a reduction. Reduction generally means a reaction in which electrons are added to a compound; the compound that gains electrons is said to be reduced. Because hydride can be thought of as a proton plus two electrons, we can think of conversion of a ketone or an aldehyde to an alcohol as a two-electron reduction. An aldehyde plus two electrons and two protons becomes an alcohol.

Aldehydes, ketones and alcohols are very common features in biological molecules. Converting between these compounds is a frequent event in many biological pathways. However, semi-anionic compounds like sodium borohydride don't exist in the cell. Instead, a number of biological hydride donors play a similar role.

NADH is a common biological reducing agent. NADH is an acronym for nicotinamide adenine dinucleotide hydride. Insetad of an anionic donor that provides a hydride to a carbonyl, NADH is actually a neutral donor. It supplies a hydride to the carbonyl under very specific circumstances. In doing so, it forms a cation, NAD+. However, NAD+ is stabilized by the fact that its nicotinamide ring is aromatic; it was not aromatic in NADH.

Reduction of Carboxylic Acids and Esters

Carboxylic acids can be converted to 1o alcohols using Lithium aluminum hydride (LiAlH4). Note that NaBH4 is not strong enough to convert carboxylic acids or esters to alcohols. An aldehyde is produced as an intermediate during this reaction, but it cannot be isolated because it is more reactive than the original carboxylic acid.

Esters can be converted to 1o alcohols using LiAlH4, while sodium borohydride ( NaBH4 ) is not a strong enough reducing agent to perform this reaction.