

Utilization of Carbon dioxide (CO₂) for the Production of Ethanol

Hizba Waheed and Arshad Hussain*

School of Chemical & Materials Engineering, National University of Sciences & Technology, Islamabad.
arshad.hussain@scme.nust.edu.pk*

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Summary: Concentration of CO₂ is increasing tremendously in earth's atmosphere which is leading to disastrous impacts like increasing earth's average temperature, melting of polar ice, rising of sea levels and other climatic effects that will result in massive drought, water shortage, agricultural losses and food shortage. Utilizing CO₂ as a feed stock for various chemicals is an advantageous solution towards this problem. New CO₂ based Fuels is developing an innovative and breakthrough technology providing a revolutionary, cost-effective solution to two global concerns: CO₂ emissions and diminishing liquid fuel reserves. CO₂ can be converted to alternate fuel by first reacting it with freshly prepared methyl magnesium bromide, CH₃MgBr (Grignard's reagent) and then reducing the resultant product into Ethanol (C₂H₅OH) by using Sodium Borohydride (NaBH₄) along with other electrophiles. The process produces 72% product yield. The product formed was characterized by using HPLC and FTIR techniques. The process can be carried out at mild conditions of temperature and pressure but keeping the moisture content minimum. The described progression will result in lessening of CO₂ and providing another option for renewable energy source.

Keywords: CO₂ utilization; CO₂ recycling; Grignard's reagent; Reduction; Synthesis of ethanol.

Introduction

In the history of development and civilization, the 20th century can be regarded as the era of hotheaded growth of population and energy consumption all over the world. There was an extraordinary jump in the inventions of new and much improved technologies along with the increasing development of man-made materials during this time. Utmost improvement was visible on the ground of transportation which is entirely dependent on efficient combustion of hydrocarbon fuels including gasoline, diesel, jet fuel etc. Extension of electric power plants, inventions of electric home appliances are more and more dependent on the production of electricity mainly from carbon-based resources such as coal and natural gas. Combustion of these solid, liquid or gaseous fuel assets cause the increasing growth of pollutant such as NO_x, SO_x and particulate matter along with greenhouse gases including carbon dioxide (CO₂) and methane [1].

Carbon dioxide is of major concern as it causes the climatic devastation like global warming by increasing the concentration of CO₂ in atmosphere, leading to increase of average earth's temperature. To avoid reinforcement of carbon dioxide it has been agreed worldwide to reduce the CO₂ atmospheric loading. Upper safety limit of CO₂ in atmosphere is 350 ppm (part per million) but all the drastic development in excessive fuel utilizing zones have made it to reach 394.39 ppm till 2011. It has been estimated that during the 21st century 3480 to 8050 Gt CO₂ will be released into the atmosphere

as compared to 1100 Gt emitted since 1850 [2]. Projections of the discussed states, yearly emission of CO₂ by 2100 ranges from 73 to 128 Gt/y while the baseline is 20.2 Gt/y [3].

Two possible ways to control CO₂ level in the atmosphere are either reducing the use of CO₂ emitting sources i.e reduction in the combustion of fossil fuels and other such sources that will release CO₂ in to the atmosphere, or we must find new methods and technologies to convert atmospheric waste into other useful products [4]. The first scheme is problematic as all our progress in the field of industries, transportation and power generation is based on combustion of carbon-based fuel. To prevent environmental damage one must capture CO₂ exhaust before it enters into the atmosphere. There are different technologies in the field to capture CO₂ but an issue is what to do with that captured carbon dioxide. One way is to dump this CO₂ in the land or ocean which will again undesirably affect land fertility and aquatic life as well. Another possibility is to consume captured flue CO₂ for productive purpose. We must search for other techniques to utilize CO₂ before it enters the atmospheric stream. In this way we can reduce CO₂ loading and thus be able to lessen its destruction towards the environment.

Research work has continuously been in progress for utilizing carbon dioxide as feed stock or as raw material for the production of beneficial products. Different chemicals like carboxylates

*To whom all correspondence should be addressed.

(RCOOR), carbonates (ROCOOR) and polycarbonates, carbamates (RR'NCOOR''), ureas, polyurethanes and various other chemicals have been prepared by different chemical reactions using CO₂ [5]. A huge amount of energy is required for the reaction as the carbon dioxide itself is a very stable compound. It is less reactive as it is a highly oxidized and thermodynamically stable compound, so high amount of energy along with highly active metal catalyst is needed to make it react. The best possible way is to convert CO₂ back into fuel, hydrocarbon or alternate fuel sources [6]. One of the profitable inventions includes conversion of exhaust CO₂ into Ethanol (C₂H₅OH). Ethanol is regarded as sustainable and energy secure fuels of the future, as its characteristics are remarkable for consumer as well as producer. With high octane number (113) Ethanol has high performance [7]. In this way we can not only reduce the amount of CO₂ from atmosphere but we can recycle CO₂ back to fuel, meeting the demand of alternate fuel as well.

CO₂ as a Significant Environmental friendly green fuel source

New CO₂ Fuels innovative technology converts CO₂ and H₂O into syngas and from it synthetic fuels for transportation. The end products are competitive with current market price. New CO₂ fuels provide a modular solution that can be easily integrated in various CO₂ emitting industries [8]. The New CO₂ Fuel system uses the CO₂ emitted by the industries and transportation facilities as feedstock and converts it into useful product that can enhance the facility's production capacity, lower its operating costs and produce new products.

Experimental

Reagents

Dry ether (ether was purchased from sigma aldrich and was dried in lab by distillation assembly), Methyl bromide (CH₃Br) by sigma Aldrich, Magnesium turnings by merck, Iodine crystals, CO₂ cylinder, Sodium Borohydride (NaBH₄) Tetra hydrofuran (THF) were provided by sigma aldrich.

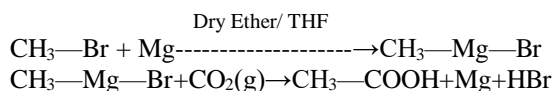
Working Up Chemicals

Hydro chloric acid (HCl, 3 N), water, Sodium hydroxide (NaOH). Reagents were purchased from sigma Aldrich and were diluted using distilling water.

Procedure

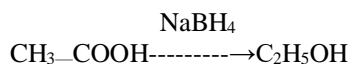
Dry apparatus was used throughout to provide moisture free atmosphere for the reaction. A small reaction tube containing a magnetic stirrer was placed inside a vacuum oven box. 50 milligrams of magnesium turnings (previously activated by stirring them for 2-3 days in Nitrogen atmosphere by adding 2-3 drops of Bromine, Br to it) along with few crystals of iodine (to activate magnesium and speed up the reaction) were added to the tube covered with a silicone septum and was placed on an electrical stirrer. A mixture of 0.5 ml of ether and 0.7 ml of methyl bromide was made in a short glass vial. The mixture was slowly added to the stirring reaction tube. A yellow reaction mixture was formed called Grignard reagent. To this freshly prepared

Grignard's reagent, continuous supply of carbon dioxide was made using tubing and was allowed to bubble through the reaction mixture for a few minutes. A cloudy appearance confirms reaction completion. The involved reactions are as follow.



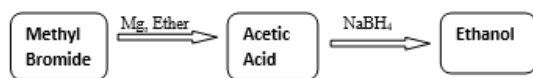
3N HCl was added to the product sample to neutralize intermediate salts formed during the reactions. The mixture was shaken vigorously. After setting down the clear solution was collected and the remaining was treated with water and 1 ml of NaOH. The final product was analyzed using analytical techniques and was found to be acetic acid.

The acetic acid formed was then poured into a three neck round bottom flask to which 4 grams of Sodium borohydride and 50 ml of Tetrahydrofuran was added. To this creamy mixture a solution of 10.6 grams of iodine in 15 ml of THF was added. The round bottom flask was stirred on an ice bath until all the gas was released from the mixture. The mixture was refluxed for 2 hours. On cooling of this mixture 50 ml of methanol was added to it. The mixture of THF and methanol was allowed to evaporate from the solution using rotary evaporator. After evaporation 40 ml of 20% KOH was added to the remaining solution. This mixture was stirred for two hours and then the KOH was evaporated using rotary evaporator.



The final product was then dried by using Sodium hydride or any other dehydrating agent. The

ultimate final product was then analyzed using different techniques. Flow diagram for the procedure is given below.



Analysis was carried out for Acetic Acid and Ethanol. Acetic acid was prepared by the reaction of Grignard's reagent with gaseous Carbon dioxide and the Ethanol was produced by the reduction of Acetic acid using Sodium Borohydride (NaBH_4) with varying conditions.

Characterization Techniques

To analyze the products formed, High Performance Liquid Chromatography (HPLC) and Fourier Transform Infrared Spectroscopy (FTIR) were used. In HPLC the components of mixtures are entirely separated on the bases of polarity of components [9]. An FTIR spectrometer instantaneously collects spectral data in a varied spectral range. For any particular type of analysis one has to provide specific conditions to the instrument [10].

Parameters for HPLC analysis

For the analysis of acetic acid, a phosphate buffer solution was prepared and was used as mobile phase. The phosphate buffer had a concentration of 20 milimole and its pH was stabilized to 2.20 by using phosphoric acid [11]. Acetic acid is weak acid and will ionize in any other mobile phase much faster. To reduce the rate of ionization and for accurate analysis it is

advised to use buffer solutions as mobile phase for HPLC. The column used for analysis was a C-18 column and the detector was a UV detector. Analysis was carried out at room temperature and the flow rate was 0.5ml/min.

For Ethanol the mobile phase used phosphate buffer of 20 milimolar strength, whose pH was adjusted to 2.2 by using phosphoric acid [12]. The buffered solution was filtered through 0.4-micron pore size cellulose membrane. It was used as mobile phase alone.

Parameters for FTIR

Samples to be analyzed are acetic acid and ethanol. Both are liquid samples. Potassium Bromide (KBr) disc is used to hold the sample in sample compartment. Lithium Tantalate, LiTaO_3 was used as the radiation source and the detector was used to analyze the sample. The analysis was made at ambient conditions. The interferograms was made for both samples and were read for further confirmations about the structure of the molecules under analysis including bond wavelength range, wave number range.

Results and Discussion

The results of HPLC analysis are in the form of chromatograms showing the plot of detector response vs time. The Standard solutions show the retention time of 1.05 min with the flow rate of 0.5 ml/min. The analysis run was made for 10 minutes. The results are shown for a single sample (60 ppm) in Fig. 1.

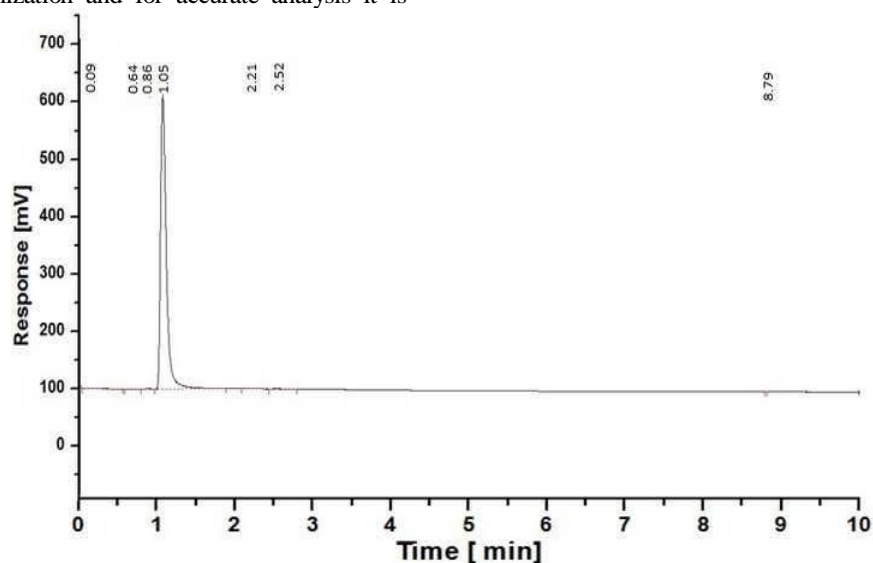


Fig. 1: HPLC chromatogram for acetic acid solution (Standard).

The same analytical method was used as for the analysis of standard acetic acid reaction and it was seen that under the same conditions the acetic acid peak was observed at the same location (Fig 2). Its peak was found exactly at the same position where standard acetic acid was found. Retention time was 1.00 min. This confirmed the formation of acetic acid by the reaction of Grignard's reagent with gaseous CO_2 .

In case of FTIR, sample were analyzed The standard FT-IR of the pure acetic acid was taken first so that the results of the reaction product can be compared to that of standard for confirmation. The

peaks of standard FT-IR (Fig. 3) are compared with that of the reaction product (Fig. 4). The FTIR results of experiment shows absorption due to O-H bond at 3387cm^{-1} C=O at 1664 and C-O bond at 1130cm^{-1} are within the same ranges as standard one, which confirms that the product formed by the reduction method is acetic acid. It was essential to have an FT-IR spectrum of pure ethanol (Fig. 5) that will work as a standard for samples of reaction products (Fig. 6). Presence of O-H bond at 3329cm^{-1} , C-H bond at 2294cm^{-1} and C-O bond at 1022cm^{-1} confirm ethanol.

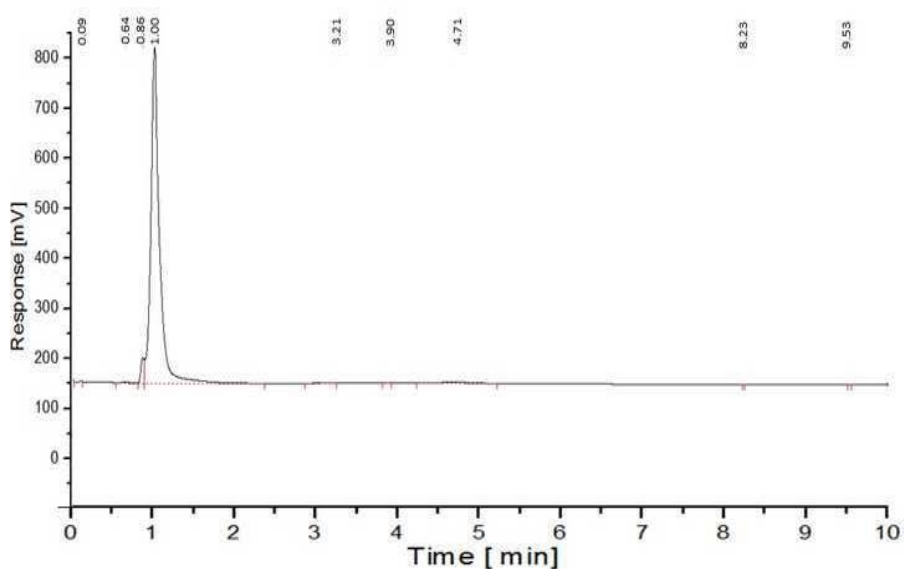


Fig. 2 Chromatogram for acetic acid solution (Test)

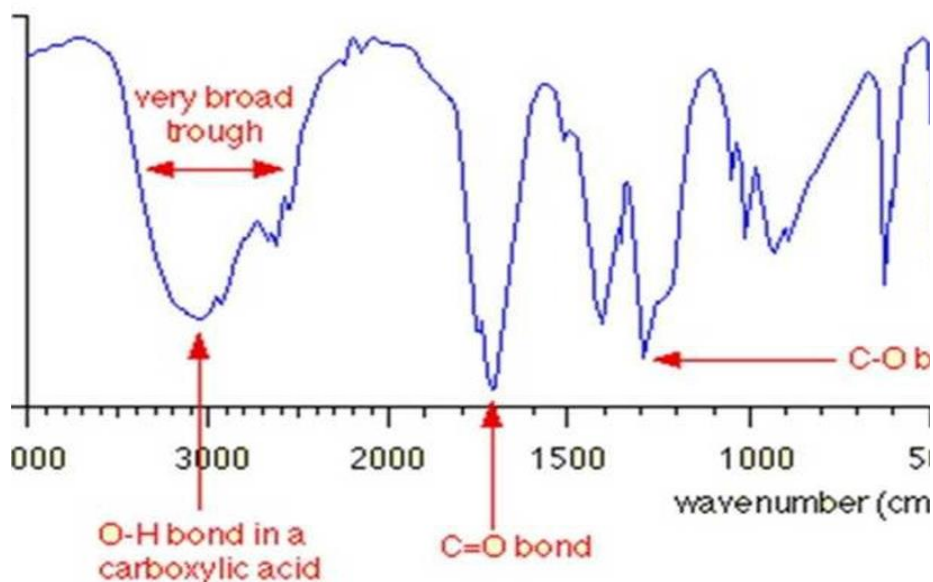


Fig. 3: FT-IR spectrum of acetic acid (Standard) [13].

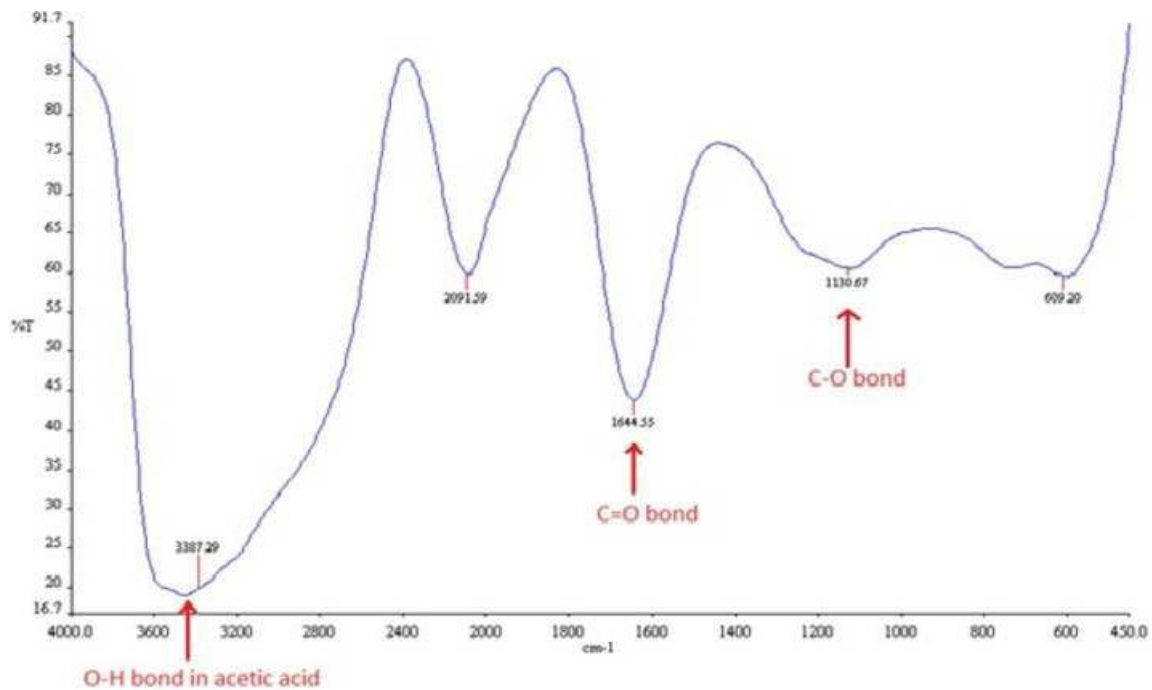


Fig. 4: FT-IR of Acetic acid (test).

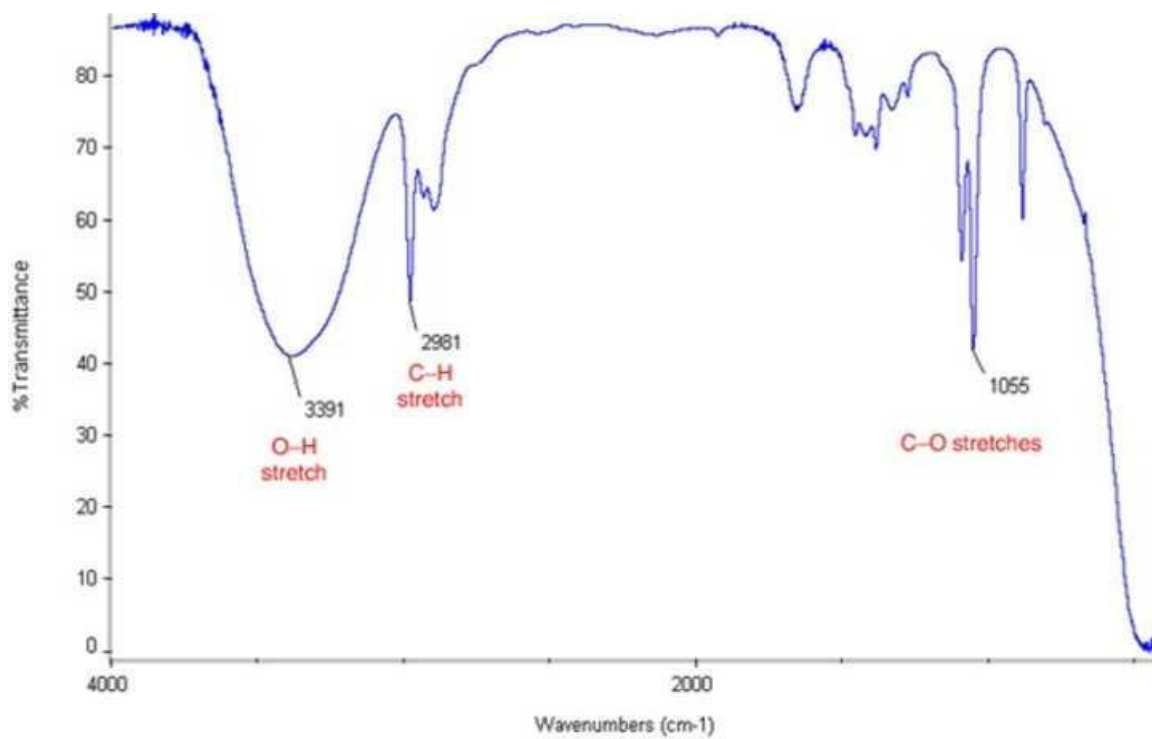


Fig. 5: FT-IR result of pure Ethanol (Standard) [14].

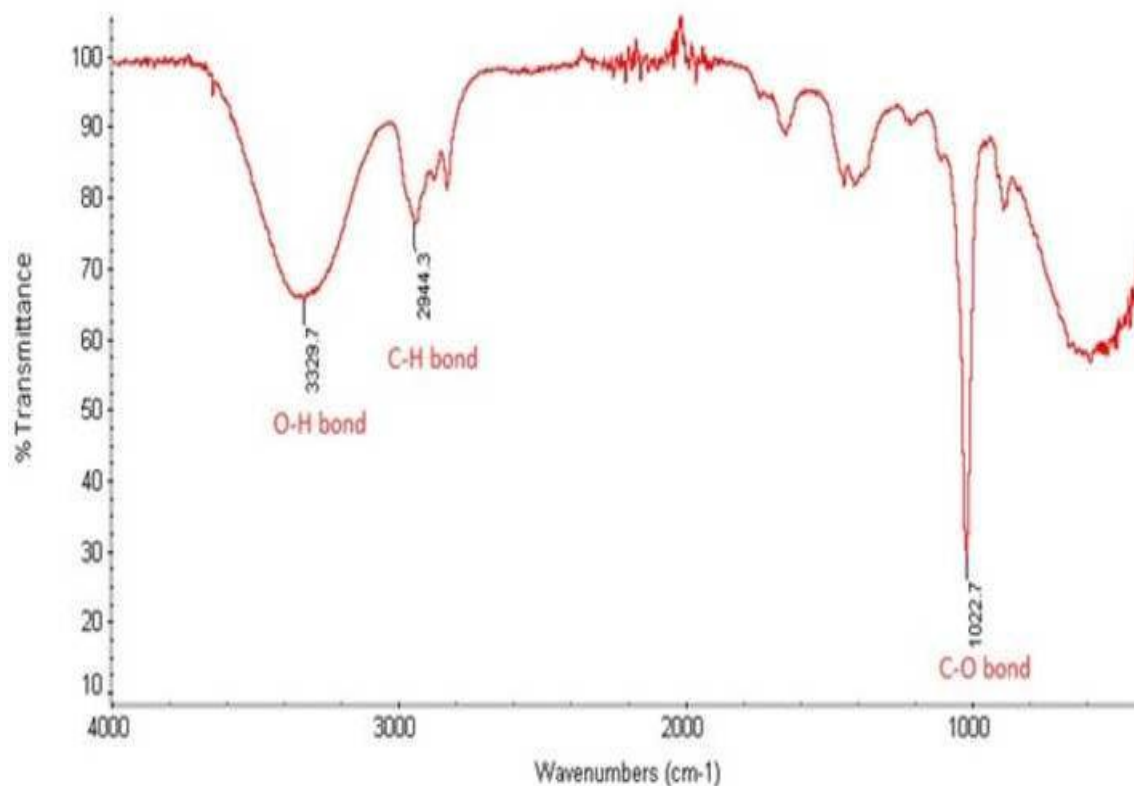


Fig. 6: FT-IR results of reduction reaction (test).

Conclusion

This research work was aimed at utilizing the waste CO₂ as a raw material for the production of useful chemicals like organic acids (acetic acid) and alcohols (ethanol). This method has high percentage yield of 72% making this process more acceptable for CO₂ lessening method. Ethanol produced as green fuel using CO₂ as a source. Here the CO₂ was used in gaseous form so that the processing of cost of CO₂ can be minimized when being used as a raw material as compared to solid CO₂. The desired products of this research work were synthesized successfully. The results were confirmed by HPLC and FTIR. The peaks of the products obtained from the experimental work were compared to that of the standard of respective products.

The research showed that that acetic acid can be produce by reacting Grignard's reagent with gaseous carbon dioxide (CO₂) and the produced acetic acid can be further reduced to ethanol by using different reducing agents working under different conditions. The aim of the research is to harness the power of CO₂ on a large scale and integrate it into the utilization cycle as a sustainable form of energy production.

Future Prospectus of CO₂ as Green fuel

Green Fuel Technologies has recently generated positive publicity for their technology, which converts CO₂-containing emissions into renewable energy sources. Carbon dioxide, CO₂, does not need to be a waste product. Instead it can be used as a carbon source, that is, a raw material for the production of sustainable green fuel such as methane, methanol, ethanol, and even synthetic diesel and gasoline. The chemical reactions required to hydrogenate CO₂ to useful fuel molecules are thermodynamically unfavorable. Therefore, huge amount of energy along with highly efficient catalysts are needed for this conversion. It is now desirable to make research in the field of catalysts and thermodynamic studies to make these reactions possible with higher yield of environmental friendly fuel and maximum consumption of CO₂ loading from atmosphere.

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