



RESEARCH ARTICLE

CO₂ CAPTURE OF OLIGOMERIC CHITOSAN OVER MONOETHANOLAMINE

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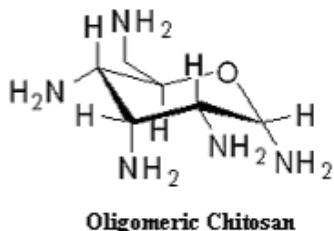
ABSTRACT

Authors synthesized the Oligomeric Chitosan material for the use of CO₂ capture and storage from industrial point sources. Oligomeric Chitosan tested for CO₂ absorption efficiency in industrial flue gas at temperature 132^oC. The results showed the absorption of 10.65 gms of CO₂ in 100 ml of 1 % solution of Oligomeric Chitosan and is higher by a factor of 21.5 at breakthrough point compared to conventional scrubbing agent Monoethanolamine(1% solution).

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INTRODUCTION

Oligomeric Chitosan was synthesized by the Authors using D-Glucose (Yeul & Rayalu, 2012). Chemical structure is shown below.



The Oligomeric Chitosan (OC) Process avoided the limitations of the Monoethanolamine (MEA) method such as CO₂ separation from flue gases: low carbon dioxide loading capacity (kg CO₂ absorbed per kg absorbent); high equipment corrosion rate; amine degradation by SO₂, NO₂ and oxygen in flue gas which induces a high absorbent makeup rate; and high energy consumption during absorbent and regeneration. When capturing CO₂ from coal combustion flue gas, the MEA process requires that SO₂ be removed first from the flue gas stream, since MEA is degraded by SO₂ and oxygen, forming irreversible degradation products. The annual cost of MEA makeup is high because of degradation, even after most of the SO₂ is removed from the flue gas in an upstream flue gas desulfurization process. It is predicted that the mostly utilized

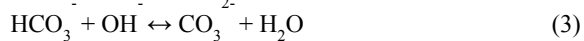
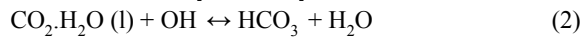
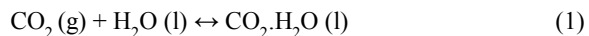
MEA Process could be replaced with the Oligomeric Chitosan Process to capture CO₂ which is exist in the flue gas. Contrasting the MEA Process, the Oligomeric Chitosan Process does not have absorbent degradation problems that are caused by sulfur dioxide and oxygen in flue gas and does not cause equipment corrosion. In concern, Oligomeric Chitosan has high loading capacity; Oligomeric Chitosan does not pose a corrosion problem; there is no absorbent degradation problem, thus reducing absorbent makeup rate; and the energy requirement for absorbent regeneration is predicted to be much lower than in the MEA process. Prior to this study, it was estimated that thermal energy consumption for CO₂ regeneration using the Oligomeric Chitosan Process could be at least 90% less than if the MEA Process is used for CO₂ absorption and regeneration. As a technique to capture and sequester CO₂, the Oligomeric Chitoammonium scrubbing process will produce Oligomeric Chitoammonium bicarbonate that will be decomposed and it will be recycled to the CO₂ capture system where carbon dioxide will be recovered and ultimately sequestered.

Chemical Absorption Phenomenon

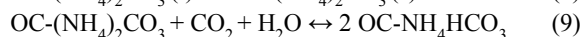
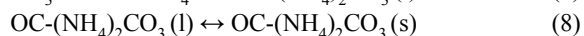
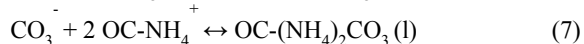
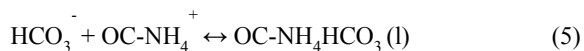
The absorption phenomenon of CO₂ in aqueous solutions can be described by equations 1-4. The amount of CO₂ that can dissolve in the solution depends on the Henry's Law constant, and the pH of the solutions [8]. The Henry's Law constant of CO₂ decreases with the increase of the temperature and ionic strength of solutions. The absorbed CO₂ can dissociate to form bicarbonate, HCO₃⁻ and carbonate, CO₃²⁻ ions. The higher the pH the more effective the absorption of CO₂. The equilibrium

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constants and the activity coefficients determine the concentration of species in solutions.



In general, a high pH solution enables a high CO₂ absorption efficiency. The absorption of CO₂ into an Oligomeric Chitosan solution can produce the crystallization of CO₂-containing Oligomeric Chitoammonium salts. These include Oligomeric Chitoammonium bicarbonate (Eq. 6), Oligomeric Chitoammonium carbonate (Eq. 8), and the co-crystallization of the those salts. These salts would crystallize once the concentrations reach their corresponding solubility products. The concentration of Oligomeric Chitoammonium ions, bicarbonate ions, carbonate ions, and CO₂, as well as the pH of the solutions influence the type of salt or salts produced.



MATERIALS AND METHODS

CO₂ absorption studies in Oligomeric Chitosan were performed directly at industry as shown in Fig. 1. The flue gas consists of 12.61 % vol CO₂ parameters shown in Table 1. The CO₂ concentration-versus-time data were used to calculate CO₂ absorption rates and to totalize the amount of CO₂ absorbed. Data was recorded every minute for the duration of a test. Carbonation of an Oligomeric Chitosan solution forms complex Oligomeric Chitoammonium and carbonate salts. The by-products are mixtures of Oligomeric Chitoammonium bicarbonate, Oligomeric Chitoammonium carbonate, complex salts of carbonate and bicarbonate, Oligomeric Chitoammonium hydroxide, and other compounds.

Table 1. Details of stack at the time of monitoring

Stack Emission Data		
Ambient Temp	⁰ C / K	35/308
Flue gas Temp	⁰ C / K	132/405
Flue gas Velocity	m/sec	14.48
Flue gas Quantity	M ³ / Sec	387.72
Flue gas Quantity	Nm ³ / Sec	294.85
CO ₂	%	12.61
Sampling flow rate	LPM	1.00

It is desirable to know the compound mix under various absorber conditions. In order to maximize the carbon dioxide loading with Oligomeric Chitoammonium ion, it would be desirable to maximize Oligomeric Chitoammonium bicarbonate formation, because one Oligomeric Chitoammonium ion will combine with one mole of CO₂,

whereas in Oligomeric Chitoammonium carbonate formation, one Oligomeric Chitoammonium ion only combines with ½ mole of CO₂. The methods of analysis were used as: Saturated barium chloride is added to an aliquot of a diluted sample to precipitate any carbonate. The development of a pink color upon addition of phenolphthalein indicates the presence of hydroxide. If present, the hydroxide is titrated with 0.1N HCl, giving hydroxide alkalinity. Bromocresol green indicator is added and titration continued to the endpoint for total alkalinity/carbonate alkalinity determination. This method presupposes the incompatibility of hydroxide and bicarbonate alkalinities (Method 2320B, Standard Methods for the Examination of Water and Wastewater, 18th edition, 1993). If no pink color develops upon the addition of phenolphthalein indicator to a sample treated with barium chloride, the absence of hydroxide is indicated. The sample is then titrated to a bromocresol green endpoint with 0.1N hydrochloric acid for a total alkalinity measurement. A second volume of sample is treated with excess 0.1N sodium hydroxide to convert any bicarbonate to carbonate. All of the carbonate is precipitated with barium chloride. The excess sodium hydroxide is immediately titrated with 0.1N hydrochloric acid to determine the bicarbonate concentration. The carbonate concentration in the original sample (before the conversion step) is calculated from the total alkalinity and bicarbonate concentrations.

RESULTS AND DISCUSSION

CO₂ Absorption

The Oligomeric Chitosan solution (1 %) was tested for CO₂ absorption several times at laboratory & at industry. The details at the time of monitoring at industry are given in Table 1. The CO₂ removal efficiency of 1% Oligomeric Chitosan & 1% MEA is shown in Figure 2. Significantly high CO₂ absorption was observed for aminated glucose. The results showed that 10.65 gms of CO₂ was absorbed in 100 ml of 1 % solution of aminated glucose and is higher by a factor of 21.5 at breakthrough point as compared to 1% solution of MEA.



Fig. 1. Monitoring of CO₂ absorption in flue gas at Industry

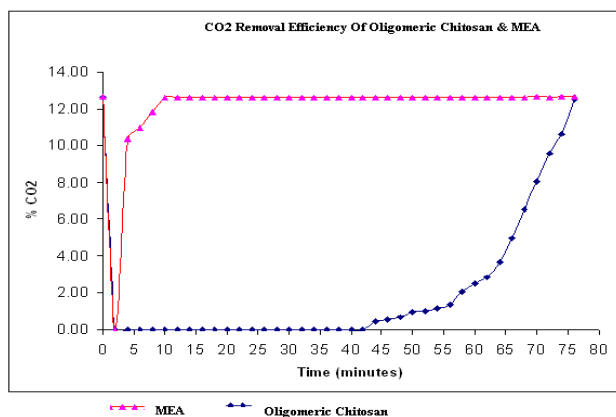


Fig. 2. CO₂ Removal Efficiency of Oligomeric Chitosan & MEA

CONCLUSION

New Oligomeric Chitosan molecule has been synthesized using D-glucose. The molecule appears to have nitrogen content of 40% and is therefore proving to be very useful for CO₂ absorption and storage. The exciting results presented herein may provide new and exciting area of research for CO₂ capture. Future research work will additionally investigate the parameters like temperature, Oligomeric Chitosan concentration, CO₂ concentration, flow rates of reactants, removals of sulfur dioxide and nitric oxides with the Oligomeric Chitosan solution.

REFERENCES

[1] Herzog, H. Editor, The Capture, Utilization and Disposal of Carbon Dioxide from Fossil Fuel-Fired Power Plants. DOE/ER-30194, 1993; Vol. 1.
 [2] Herzog, H., E. Drake, and E. Adams, ed. CO₂ Capture, Reuse, and Storage Technologies for Mitigating Global Climate Change, A White Paper Final Report. January, 1997. DOE Order No. DE-AF22-96PC01257.

[3] Duncan, Joanna Electro-Catalytic Oxidation (ECO): Results from Pilot Scale Testing of Simultaneous NO_x, SO₂, Hg and PM_{2.5} Removal at First Energy's R. E. Burger Plant, Proceedings of 20th Annual International Pittsburgh Coal Conference, Pittsburgh, PA 2003.
 [4] NPCC. Study on CO₂ Sequestration by Spray Concentrated Aqueous NH₃ and Production of Modified NH₄HCO₃ Fertilizer - a Proposal for US-China joint research. State Engineering Technology Research Center of Combustion of Power Plants (NPCC), China. May, 2000.
 [5] Bai, H. and A.C. Yeh, Removal of CO₂ Greenhouse Gas by Ammonia Scrubbing. Ind. Eng. Chem. Res., Vol. 36, No. 6, 1997.
 [6] Yeh, A.C. and H. Bai, Comparison of Ammonia and Monoethanolamine Solvents to Reduce CO₂ Greenhouse Gas Emissions. The Science of Total Environment, pp 121-133, 228, 1999.
 [7] J. T. Yeh, Personal Communication on research data of CO₂ capture by ammonia solution. NETL/DOE, 2000.
 [8] Private communication, Dr. S. G. Chang, Lawrence Berkeley Laboratory, Oct. 2003.
 [9] Kohl, A and R. Nielsen, Gas Purification, 5th edition, Gulf Publishing Co.
 [10] Resnik, K.P., Yeh, J.T., and Pennline, H.W. Oligomeric Chitosan Process for Simultaneous Removal of CO₂, SO₂ and NO_x. In print in Int. J. Environmental Technology and Management. 2004.
 [11] Yeh, J.T., Resnik, K.P. and Pennline, H.W. Regenerable Oligomeric Chitosan Process for CO₂ Sequestration. Prepr, pap-Am. Chem. Soc., Fuel Chem. 2004, 49(1).
 [12] Goff, G.S. and G.T. Rochelle. Oxidative Degradation of Aqueous Monoethanolamine in CO₂ Capture, AIChE Annual Meeting, 2002.
 [13] Yeul Vijay & Rayalu Sadhana, Int. conf. RDEIA-IACM 2012
