

**A Thermal Swing Absorption Process
for Production of Oxygen-Enriched Combustion Air**

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Abstract. A thermal swing absorption (TSA) process for the production of oxygen-enriched combustion air is described. The process is designed to achieve a ca. 50% fuel efficiency savings by the use of greater than 50% oxygen-enriched air in coal-fired boilers. The TSA process described has three components: an inorganic oxygen-carrying compound (carrier), a solution formulation of the carrier (with supports, promoters, and solvents), and a flow-system reactor with oxygen concentration monitoring. Criteria necessary to success of the process are identified. A literature search for appropriate compounds is summarized. Two compounds are identified, synthesized, formulated and tested in the TSA process. The compounds performed successfully over four absorption/desorption cycles. Goals for further improvements are stated.

Introduction

It is reported¹ that oxygen enriched combustion can substantially improve the thermal efficiency of a combustion system. Union Carbide found that in furnaces with combustion temperatures above 1100°C, an oxygen enrichment of 50 to 100% would result in a 40 to 60% fuel savings. The cost savings and thus economic feasibility of oxygen enriched combustion is sensitive to both fuel prices and the cost of producing oxygen. As an added advantage, the use of oxygen enriched combustion air (OECA) will also minimize NO_x formation.

In a recent study² it is reported that thermal swing absorption (TSA) using a solution absorbent offers a potentially viable option for producing low cost OECA for industrial use. The TSA process consists of using a chemical in solution which is capable of absorbing oxygen at low temperature (say 23°C) and desorbing it at higher temperature (say 65°C). These temperatures can be obtained by cooling with ambient air and heating with flue gases. The use of waste heat from combustion gases would make this process economically very attractive.

A solution absorbent system consists of a reversible oxygen-binding chemical compound dissolved in a formulation of solvents and promoters. Four major criteria may be applied to the

absorbent solution. First, it should have a high, reversible and selective affinity for oxygen at room temperature or slightly above, and a lower affinity at a higher temperature (generally greater than 50°C), so that it will absorb and desorb oxygen. Second, the absorption process should happen at a reasonable rate. The solution should have a reasonable lifetime (i.e. it should be possible to cycle the absorbent many times without experiencing degradation). Finally, it should absorb the maximum weight of oxygen per unit weight of solution; this generally implies that the compound be quite soluble in the solvent and promoters.

It is important to note that while many compounds have been observed to have a reversible affinity for oxygen,³ many physical properties of the compounds which affect their suitability for a TSA formulation are not known. Indeed, few solution absorbent TSA systems have been described.⁴

In this paper, we describe a literature survey of compounds for TSA formulation, and the identification of two compounds for study. The preparation, formulation, and testing of these two in a TSA apparatus is reported. Finally, the significance of the oxygen absorption performance and plans for the future are mentioned.

Experimental

General. Reagents and solvents were obtained from commercial sources (analytical reagent grade) and used as received. *N,N'*-bis(salicylidene) *o*-phenylenediimino cobalt(II) (also known as Salcophen or CoSalophen) was purchased from Aldrich Chemical Co. and used as received. NMR spectra were obtained on a Bruker AM-360 spectrometer. Infrared spectra were obtained on Perkin-Elmer 283B spectrometer.

Preparation of *N,N'*-bis(salicylidene) ethylenediimino cobalt(II).⁵ I. *N,N'*-bis(salicylidene)ethylenediimine (salen). Freshly distilled salicylaldehyde (7.1 mL, 0.067 mol) in 95% ethanol (33 mL) was heated to a boil with stirring.

Ethylenediamine (2.2 mL, 0.0335 mol) was added and the solution was let cool. The resulting yellow precipitate (5.51 g, 61% yield) was filtered and dried under vacuum for 3 h. Proton NMR and elemental analysis (C, H, N) agreed with expected values.³

II. *N,N'*-bis(salicylidene) ethylenediimino cobalt(II) (Salcomine or CoSalen). Salen (2.74 g, 0.0102 mol) and sodium acetate (0.031 g) were dissolved in ethanol (31 mL), water (6.7 mL) and 1.0 M aqueous sodium hydroxide (24.3 mL). The mixture was brought to a boil with stirring and cobalt (II) chloride hexahydrate (2.43 g, 0.0102 mol) was added precipitating CoSalen as a brown product which was separated by filtration and washed with water until the washings were colorless. The cake was dried at 110°C for 3 h under reduced pressure, yield 2.75 g (83%). The elemental analysis (C, H, N) and IR spectrum (KBr pellet) agreed with expected values.

Measurement of Oxygen Absorption Under TSA Conditions. The measurement system is shown in Figure 1. Air (A) was passed through a needle valve and a calibrated Hastings mass-flow meter (B) to establish and measure the air flow rate. The air was bubbled through the reactor (D) where absorption and desorption take place. The effluent of the reactor was passed through an Infrared Industries IR-2200 Oxygen Analyzer (E) and then exhausted into a hood. A bypass line (C) around the reactor allowed for calibration and check of the analyzer. The reactor consists of an outer metal jacket around a glass reaction vessel fitted with a rubber stopper through which the gas inlet, gas outlet, thermometer and thermocouple were passed. The reactor was alternately cooled in each absorption cycle and heated in each desorption cycle. The gas inlet consisted of a glass line with a frit attached to promote contact of the gas with the liquid.

The data from the oxygen analyzer, mass flow meter, and thermocouple were collected using an IBM PC/XT with the labtech/Notebook data acquisition system. The amount of oxygen absorbed and desorbed was calculated by integrating the product of the oxygen concentration and flow rate over the cycle.

Results and Discussion

Selection of Candidate Compounds. The literature was surveyed based on the above criteria, resulting in a tabulation of cobalt (II) compounds considered candidates for the TSA process. Table I is partial listing of these compounds.

Parameters found in the literature include the solvent and concentration of the formulation (columns 6 and 4). These are important to the fourth criterion above, because they provide information on the solubility of the cobalt complex. Clearly, those oxygen-binding compounds which are more soluble may produce a solution which contains more of the oxygen-binding ingredient and therefore has a greater oxygen absorbing capacity.

The nature of the axial base (column 5) affects the oxygen affinity of the complex (first criterion), by changing the electron density at cobalt, which is the active site for oxygen binding. Other parameters important to the first criterion are the temperature, binding ratio (mol Co:mol O₂), and oxygen affinity (log K_{O₂}). These parameters all provide information on how well the complex would hold and release oxygen during a TSA cycle.

These data are insufficient to determine if the compounds are suitable for the TSA process, however. Some of the data needed are oxygen affinities at higher temperatures (first criterion), maximum solubilities in a range of solvents (fourth criterion), rate of oxygen binding (second criterion), and stability to oxidative degradation (third criterion).

Compounds #1 and #2, CoSalen and CoSalophen (also referred to as salcomine and salcophen, respectively), were selected for further study to obtain some of the above data. They were chosen due to their relatively high oxygen affinities and reasonably

high solubilities. While DiCobalt-o-bistren, #4, has a higher oxygen affinity, its low concentration value of 2×10^{-4} M is not practical.

Synthesis and Testing. CoSalen was prepared by modification of a literature procedure while CoSalophen was purchased. CoSalen and CoSalophen were tested for solubility in various solvents. Dimethylsulfoxide (DMSO) was found to be most suitable, giving a high concentration, 0.03 M.

The formulations were tested in the TSA system, giving the results of Table II. In Table II, the first cycle for each compound may be disregarded, as the solutions were prepared in air so that the oxygen content of each solution at the start was unknown. Subsequent cycles give similar oxygen capacities in the absorption and desorption cycles, indicating that all oxygen bound is released. Thus, oxidative degradation is not occurring, because no oxygen is consumed in the cycles. Further, the oxygen capacities are similar from cycle to cycle, indicating that no other deterioration of the absorber is occurring over these cycles.

The utilization value indicates what fraction of the cobalt complex carries oxygen. This value is determined by the difference between the oxygen affinities at 65°C and 25°C, for CoSalophen (between the affinities at 65°C and 22°C for CoSalen). These are related to the $\log(K_o)$ values of the complex.

Sample plots of oxygen absorption/desorption versus time are shown in Figures 2 (CoSalen) and 3 (CoSalophen), for the fourth cycle of each measurement. From these the rate of oxygen absorption and desorption may be approximated. For CoSalen, the absorption time is ca. 3 min and the desorption time ca. 4 min, while for CoSalophen it is ca. 4 min for absorption and 3.5 for desorption.

Future work will concentrate on improving the oxygen capacity of these TSA compounds. Several approaches will be taken. The solubility of the oxygen absorbing compound will be increased allowing a higher concentration of oxygen absorber per gram of solution. The utilization will be increased by increasing the desorption temperature and increasing the oxygen affinity of the compounds. Finally, the number of cycles will be increased to determine the lifetime of the compounds.

Conclusion

The thermal swing absorption process has been demonstrated using cobalt (II) Schiff-base complexes formulated as solution absorbents in a flow system. Parameters of the system have been determined for two cobalt complexes over four absorption/desorption cycles.

References

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Table I. Candidate Compounds for Oxygen Production by the TSA Process

No	Chemical (A) (Mol.Wt.)	Structure (A)	Conc. of (A)	Axial base (B)	Solvent (C)	Temp (°C)	Ratio (Co:O ₂)	gO ₂ /g(A)	gO ₂ /g soln. (A+B+C)	log KO ₂	Ref. #
1	CoSalen (325)		0.01M	4-Methylpyridine (2M)	diglyme	25°	2:1	0.0492	1.7x10 ⁻⁴	0.91	1,2
2	CoSalophen (377)		0.012M	4-Mepy (2M) 4-CNpy (1M) Py (2M) DMAP (2M)	"	25	1:1 2:1	0.0849 0.0424	4.098x10 ⁻⁴ 2.05x10 ⁻⁴	-2.74 -2.82 -2.81 +1.04	"
3	CoOCH ₃ Salen (355)		0.010M	4-MePy (3M)	"	10	1:1	0.0901	3.4x10 ⁻⁴	-1.68	"
4	DiCobalt- <i>o</i> -Bistren (645)		2x10 ⁻⁴ M	NaOH	H ₂ O	25	1:1	0.0496	6.4x10 ⁻⁶	4.57	3
5	Co(S-Me)en(NO ₃) ₂ (358.8)		0.075M	Et ₂ en (2M)	Formamide	25	1:1	0.0892	3.49x10 ⁻⁴	No data	4
6	2,4,6-Tri(mesityl)-phenol (448)		0.0372M	0.3g K ₂ C ₂ O ₇ butanolate	<i>i</i> -butanol	20	1:1	0.07142	1.47x10 ⁻³	No data	5

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Table 11. Oxygen Absorption Data

Compound	Conc. mol/L	Solution Mass, g	Cycle No.	Bath Temperature, °C		Oxygen Capacity, $\times 10^{-4}$ g(O ₂)/g(soln)		mol(O ₂)/mol(compound) Absorp	Utilization, mol(O ₂)/mol(compound) Desorp
				Absorp	Desorp	Absorp	Desorp		
Cosalen	0.03	218	1	22	65	0.890	1.54	.110	.191
Cosalen	0.03	218	2	22	65	1.81	2.00	.225	.249
Cosalen	0.03	218	3	22	65	1.80	1.90	.224	.235
Cosalen	0.03	218	4	22	65	1.81	1.83	.225	.227
Cosalophen	0.03	219	1	25	65	5.05	1.15	.063	.144
Cosalophen	0.03	219	2	25	65	1.26	1.29	.158	.162
Cosalphen	0.03	219	3	25	65	1.16	1.30	.145	.163
Cosalphen	0.03	219	4	25	65	1.15	1.23	.142	.153

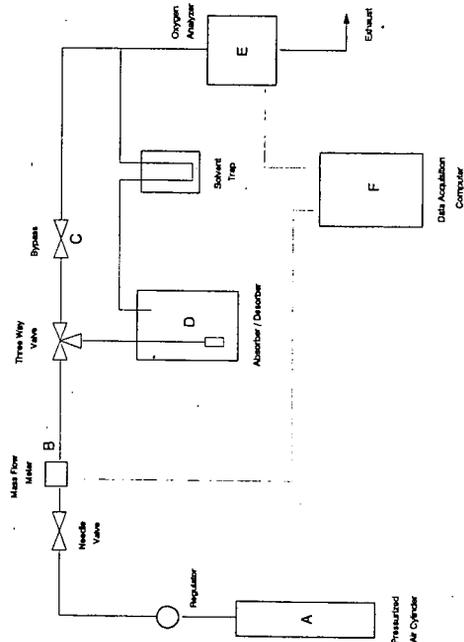


Fig. 1: Oxygen Absorption / Desorption Experimental Set-up

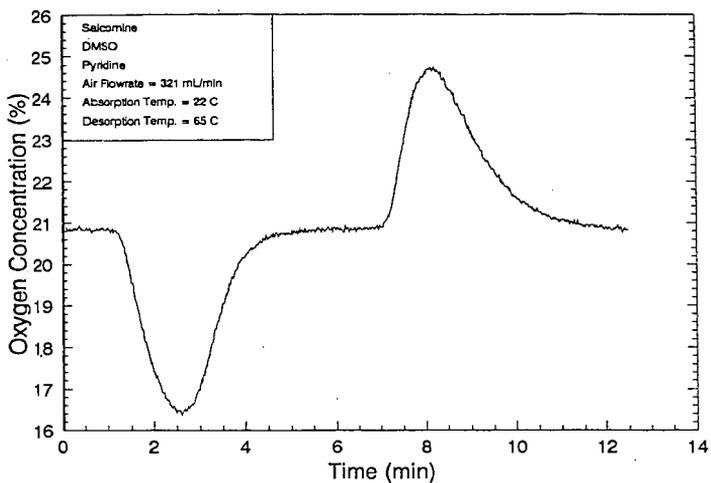


Fig. 2: Oxygen Absorption / Desorption for Salcomine

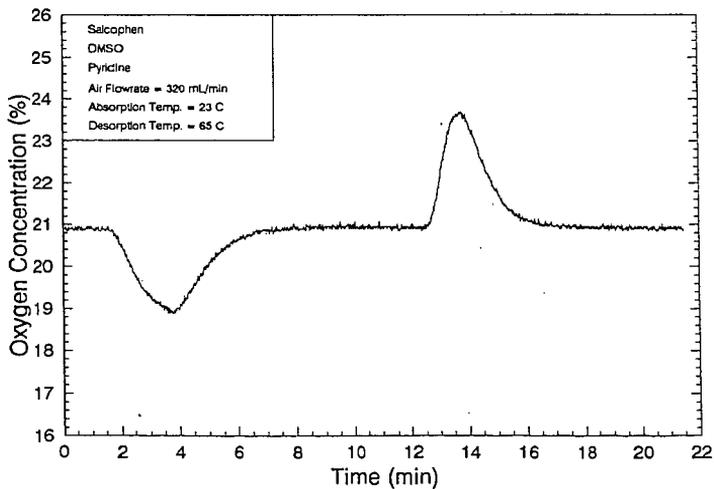


Fig. 3: Oxygen Absorption / Desorption for Salcophen