Virtual Sensing and Sensitivity Analysis of Sour compression technique (SCU) of a Cement Manufacturing Plant

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DEDICATIONS

To my very Supportive, Loving, and Caring Family

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ABSTRACT

The cement industry is a prominent source of CO_2 emission to the environment. To minimalize the pernicious influence of the CO_2 emission on the environment, CO_2 capturing has been the focus of research. Sour compression technique (SCU) is a reliant and commonly used method for CO_2 absorption. For a stable and efficient operation of SCU, a robust sensing and control system is vital. The data-based model also termed as databased virtual sensors have been attracting attention in the process industry for enhancement and replacement of the conventional hardware sensors such as flow meter, pressure gauge, and composition analyzer. In this study, a databased virtual sensor is designed to relate process conditions such as pressure, temperature, and flow rate to the carbon-capturing capability of SCU. An Aspen Plus based model of the SCU comprising of CO_2 capturing, desulfurization and denitrification processes was developed. The process model was converted to dynamic mode through the interfacing of MATLAB-Excel-Aspen to achieve the behavior of real-time cement plant operation. Five hundred fifty (550) datasets were generated that consisted of process conditions and their corresponding values of the CO_2, SO_2 and NO in the process outlet streams. The data was used to develop the virtual sensor through ensemble learning, *i.e.*, boosting. Prediction performance of the virtual sensors for CO_2, SO_2 and NO was 98.86%, 99.63% and 99.7%, respectively. Moreover, a sensitivity analysis was done on datasets to checkout any influence of input or set of inputs on output. Variance based SOBOL and Fast Amplitude Sensitivity Analysis (FAST) are techniques to figure out the impact of inputs. The results demonstrated that the proposed framework could be used effectively for composition monitoring of CO_2, SO_2 and NO in the exhaust stream of a cement production plant.

Keywords: Sustainability; soft-sensors; process flow sheeting; greenhouse gases; process industry

List of Abbreviations

SCU	Sour Compression Unit
CO_2	Carbon Dioxide
O_2	Oxygen
H_2O	water
N_2	Nitrogen
H_2	Hydrogen
NOx	Nitrogen Oxides
SOx	Sulphur Oxides
HF	Hydrogen Flouride
HCL	Hydrogen Chloride
Hg	Mercury
CH_4	Methane
FAST	Fourier Amplitude Sensitivity Analysis
LSBoost	Least Square Boosting
GHG	Green House Gas
ppm	parts per million
ETC	Energy Transition Commission
IEA	International Energy Commission
CCS	Carbon Capturing and Storage
PZ	Piperazine
de-SOx/de-NOx	de-sulphurization/de-nitrification
IoT	Internet of Things
Gt	Giga Ton
RDF	Refused Derived Fuel
EU	European Union
RES	Renewable Energy Sources
PCC	Post-Combustion Capture
COE	Cost of Electricity
NCCC	National Coal capturing center
Na_2CO_3/$NaHCO_3$	Sodium-carbonate/Sodium-bicarbonate

MLP	Mixed Linear Programming
mg/Nm^3	milli-gram/normal-meter-cube
lb mol	pound-mol
cum/h	cubic-meter/hour
TSA	Temperature Swing Absorption
C-Coeff	Correlation Coefficient
IL	Ionic Liquid

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Chapter 1

Introduction

The ominous challenge for the present human race is climate change as anthropogenic greenhouse gas emission (GHG); CO_2, CH_4, NOx, and SOx have increased global temperature by 1^{o}C since the preindustrial era [1]. To lessen climate change, UN members have signed several agreements, *i.e.*, Paris agreement, Kyoto protocol, Copenhagen accord, etc. At the instant, atmospheric CO_2 concentration is around 400ppm much higher than the preindustrial period (280 ppm). The Energy Transitions Commission (ETC) brought together a broad, diverse group of energy-related personnel. That group of leaders is energy producers and users, different industrial equipment suppliers, bankers and investors, non-profit establishments, and scholars from every corner of the world. ETC intends to speed up transformation towards low-carbon energy systems that support robust financial development and bound the increase in worldwide temperature to well below 2°C and to maintain up-to 1.5°C. In November 2018, the ETC put forward the agenda of achieving net-zero carbon emission, specifically tougher to decrease sectors by the middle of this century.

Global climate change occurs regularly due to numerous factors like volcanic eruptions, earth orbit changes, and change in oceanic currents, sun's intensity, and greenhouse gas emissions (GHG). GHG, especially CO_2, NOx, SOx, and CH_4, have increased the global temperature since the preindustrial era. The most recent global rise in temperature due to greenhouse gas emissions is a hot topic among scientists and triggered governing bodies worldwide. To lessen the global temperature international energy agency (IEA) projects, 50% reduction in industrial CO_2 emission than 2005 emissions will limit global warming to 2°C to 3°C [2]. These GHG emissions results in the production of off/onshore gas processing, H_2 production from biomass or natural gas, emissions from transport vehicles, clinker production for cement grinding and steel production, *etc*.

The United Nations Intergovernmental Panel on Climate Change (IPCC) in 2006 provided guidelines that negative carbon emissions must be allocated in National GHG inventories, but this preposition yet to be reordered into the current policy

framework. For instance, in the third phase of EU ETS between 2013 to 2020, those CCS installations that operate on biomass are omitted from the current policy. As policy doesn't recognize the potential of achieving negative emissions by joining CCS and biomass. Carbon capturing in biomass-based industries must also be accredited for doing so.

The greenhouse effect is a phenomenon where CH_4, NOx, SOx, water vapours, *etc*., blocks outgoing infrared waves and consequently, make the lower atmosphere more temperate. CO_2 is to be blamed because of its central role in global warming and abundance. The serious concerns because of GHG emissions are melting of polar glaciers resulting in increased sea level and disorder in precipitation, frequent acid rains, increased frequency and intensity of extreme weather conditions, increased vector of disease, and extinction of already endangered species [3].

Among the top-emitting CO_2, *i.e.*, transportation sector, Aviation sector, oil and gas Refineries, and cement. The cement industry is one among other leading sources of CO_2 emission to the environment. Clinker production makes up to 2.2 Gt of CO_2 emissions in 2014, which encompassed 1.2 Gt and 0.75 Gt of emissions from process and combustion, respectively. So, the process-based emission of CO_2 in clinker production, it is challenging due to the unavoidable process conditions. As far as current cement quality is concerned, newly updated chemical reactions and combustion mechanisms for clinker production are meagerly carbon-intensive. Therefore, to eliminate process-wise emissions its necessary to employ some carbon-capturing technology. The present-day worldwide demand for cement is nearby 4.2 billion tons per annum and is anticipated by the IEA's Reference Technology Scenario to produce to 4.7×10^9 tons by 2050 [4].

This is highly accepted across the globe that implementation of any carbon capturing and storing (CCS) installations will be abundant at the point source. The primary source can be power generation houses or steel, natural gas, iron, and cement production industries. The implementation of CCS is due to two main reasons, which are, firstly, 60% of global emission is from these point sources, and it will remain to continue till 2030 and after that and, besides, there is enough extent of technological and manufacturing expertise that is linked with implementation of such technologies.

So, to maintain the average global temperature within temperature limit of 2°C as stated above, CCS technologies can easily be implemented with fewer uncertainties and risks along with other mitigating options like renewable energy and process optimizations and revamps. For the time being, the primary gradient for CCS application is CO_2 usage in enhanced oil recovery at any well. Pressurized CO_2 is injected into the well, causing oil viscosity to drop, resulting in increased oil flow.

To abate the pernicious influence of CO_2 emissions on humankind and the environment, CO_2 capturing has been the focus of research. So far, CO_2 capturing is a concern; there are many techniques to get pure CO_2, and these are in use accordingly. Two main CO_2 capturing mechanisms are pre and post-combustion techniques. The pre-combustion technique is not feasible in the cement production process as CO_2 emits after fuel combustion and calcium carbonate calcination. Post-combustion capturing is a unique technological method for capturing small concentration CO_2 from flue gas and preparing unpolluted CO_2 stream (around 95%). Post-combustion capturing is the most feasible option to retrofit into the existing facility so it can be carried out with minimum risk. However, the capital cost, operating cost and maintenance cost to carry out CCS is high because of the CO_2 in flue gas has low pressure and concentration.

1.1 CCS in Industries

Some operational CCS are mature enough like compressed CO_2 transportation, integration within processing plant, EOR and high purity point source capturing but they are very few and limited. Some capturing techniques and many catalysts for CO_2 capturing ability are still under investigation phase. So, much of large scale demonstration is needed to overcome technical deficiency and experience.

Capturing technology greatly affected by price tag and readiness of that technique itself. Also, some process industries also capture CO_2 as a part of process requirement like production of urea from ammonia. Several other techniques of carbon-capturing in different industries like iron and steel, cement production and petroleum needs additional techniques to concentrate dilute streams of carbon-containing streams. Some of the separation processes which are in use are absorption, adsorption,

temperature or pressure swing adsorption, gas liquefaction and membrane separation. They come under three main categories:

- **Removal from diluted streams,** in most of the post-combustion cases like in cement production and power generating plants low concentrated CO_2 stream, is treated with some certain sorbent. Such sorbent will remove CO_2 selectively from the gas mixture.
- **Removal from oxy-fired streams,** combustion in the presence of somewhat pure oxygen results in most concentrated CO_2 stream produces. It is ready for transportation after removal of usual contaminants and sulphurous compounds removal.
- **Pre-process removal,** similarly for such type of capturing fuel is subjected to mild oxidation in which syngas is produced. Then through the help of water-gas shift reaction CO_2 and hydrogen gas is produced. In this way, CO_2 is readily available at a higher concentration for easy removal.

Currently, CO_2 capture strategies are universal and commonly discussed subjects. Standard alkanolamines and sterically slowed down amines are the most commonly used industrial solvents for CO_2 capture. DEA, MEA, and MDEA can be called primary, secondary, and tertiary amine solvents, respectively, basic alkanolamines. Monoethanolamine (MEA) is considered a benchmark for the selection of chemical solvents from starch. However, MEA is potentially oxidized as oxygen and SOx require more intensive care. Lately, cyclic diamine, particularly piperazine (PZ), was developed to improve MEA's rapid reaction kinetics and improved thermal and oxidative degradation resistance. However, it can also react with NO_2 in flue gas, similar to other amines, limiting absorption ability. Like other alternatives to CO_2 capture, ammonia-based systems measuring aqueous and ice-cold ammonia is found. This method has many benefits over amine-based systems, such as resistance to oxidative degradation, CO_2 absorption, low manufacturing costs, and durability. A few industrial-based CO_2 removal facilities are now available but they are not yet developed enough for CCS and few of them are in demonstration phase as shown in Table 1.1.

Table 1.1: Industrial based CCS and their maturity level

Industries	Employed technology	Expected time frame maturity of CCS
Highly pure streams	Ammonia Based	Currently mature
	Gas processing	Currently mature
	LNG production	Currently mature
	Coal synthesis	Currently mature
Cement	Chemical Absorption	2015-2020
	Oxy-fuel	2030
	Carbonate Looping	2030
Iron and Steel production	Post-combustion blast furnace	2020
	Oxyfuel blast furnace	2020-2030
	Gas DRI	2020
	FINEX steelmaking process	2020-2030
	HIsarna steelmaking process	2030
Oil refineries	H_2 production from gas reforming	Mature
	Gasification residues for H_2 production	2015-2020
		2030
	Fluid catalytic converter	2020
	Process-based heat	

Solid solvents such as water are used in CO_2 purification, aside from organic solvents. For physical solvents, Henry 's Law shows the high-pressure gas absorption. This technique is currently used mostly in chemical processing processes such as syngas, hydrogen, and natural gas extraction. Therefore, the treatment of NOx and SOx first-hand is unavoidable for CO_2 absorption. It has an advantage over other strategies among a few Sour Compression Unit (SCU) technology, as it uses water to absorb NOx and SOx in the flue gas. In the opposite, specific methods to avoid standard contaminations (H_2O, O_2, N_2, SOx, and NOx) are generally based on the key steps: a step of de-SOx / de-NOx and absorption by water, a systematic distillation unit or a two-stage flash unit, in order to remove volatile gas from the left.

In consideration of the cement sector, CCS technologies are not expected to be available by the year 2020, also as per IEA/WBCSD, 2009 it is prone to increase its

production cost from 40% to 90%. Oxy-fuel technology appears to be very promising but still, there is plenty of room left for extensive research for integration and compatibility with clinker production. So, one of the well-known projects at small scale was demonstrated by CEMEX which was employed on post-combustion capturing. As from Figure 1.1, the projected CO_2 emission from cement sector will increase from 1.9Gt to 2.2Gt. This was funded by the US department of energy but due to high capital cost and time constraints its wasn't carried out on the industrial scale.

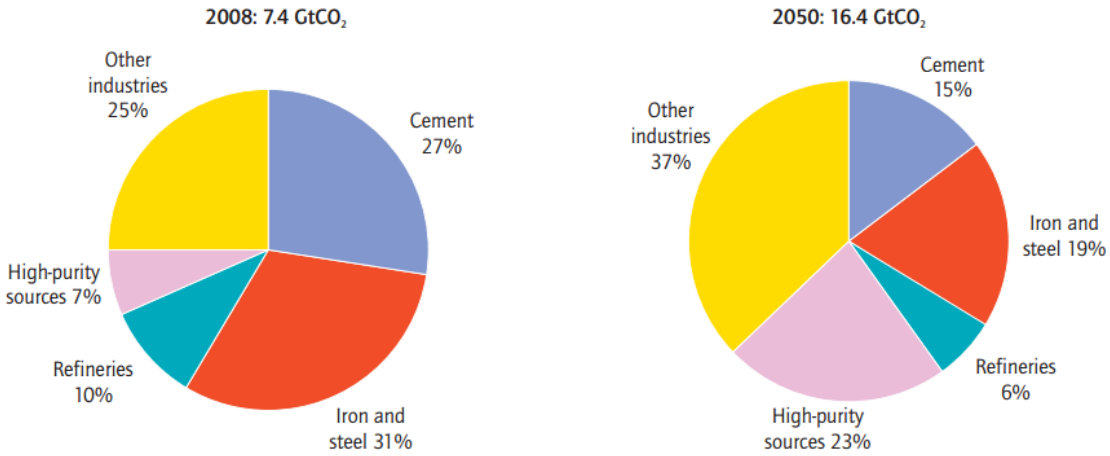

Figure 1.1 Projected CO_2 emissions by 2050

The term Industry 4.0, or fourth industrial revolution, indicates the outline of usage of information technologies in plants. This term is used in the context of the digital transformation of the industry. This broad term refers to the usage of cyber-based physical systems, the Internet of things (IoT), cloud computing, applications of deep learning, artificial intelligence, and machine learning. The outline of Industry 4.0 provides upsurge to what is called "Smart Factory." These cyber-physical systems are going to be used for monitoring process industries. Acknowledgements to IoT, diverse systems can interconnect with each other, allowing collaboration with other human systems and operators in actual. With the help of cloud computing, cyber physical-based big data can be stored centrally. Lastly, in industry 4.0, different machine learning techniques enable us to comprehend existing patterns in particular data. However, the introduction of machine learning techniques in production and process methods can be enhanced and understood shrewdly. This achievement and evaluation

can be carried out by collecting data during the production process. Through such evaluations, state-of-the-art processes are obtained that can adjust production variations uninterruptedly. Thus, the various distinct processes are not only fairly inked but can also be adjusted.

The usual practice in processing plants is that they are heavily instrumented with the help of numerous measuring instruments for the sake of optimum process conditions. So, the main objective of sensors is to send data for better monitoring of the process and to control it. About two decades ago scientists started to make predictive models based on the stored data of a certain process industry [5]. These predictive models are called "Soft Sensors". This term is a combination of the two words “software” as it is based on computer-based software and "sensor" as it delivers the same information about the process just like hardware-based instruments. Sometimes these predictive models are also called *inferential sensors, virtual online analyser and observer-based sensors.* Generally, soft sensors are divided into two main types model-driven and data-based soft sensors. The model-driven soft sensors primarily based on the First Principle Models (FPM). FPM in the process delineates physical and chemical behaviour. Most usage of these models is for the designing and planning in processing plants, in turn, its one of their drawback that designing can't be solely used for such purpose. On the other hand, data-driven soft sensors are getting much reputation in process industries. They are based on real plant data and thus are more efficient in showing a true picture of the process.

To serve this purpose and for a stable and efficient CCS operation, a robust sensing and control system is vital. In this study, data-based virtual sensors analysis is carried out by ensemble learning method, boosting, for prediction performance of SOx/NOx removal and CO_2 recovery. A databased virtual sensor is designed to relate process conditions, *i.e.*, temperature, pressure and flow rate, *etc*., to the carbon-capturing capability of SCU. Ensemble learning is used to overcome the variance and overfitting of data. An Aspen Plus based model of the SCU comprising of CO_2 capturing, desulfurization and denitrification processes was developed. To capture the behavior of real-time cement plant operation, the process model was converted to dynamic mode through the interfacing of MATLAB-Excel-Aspen.

1.2 Aims and objectives

The main objective of this thesis is to present the viability of Carbon capturing technique from the flue gases of the cement industry. This will be carried out firstly removal of SOx and NOx by water absorption then the removal of moisture content at pure CO_2 separation from residual gases through cryogenic unit. To fulfil the aim study is done on the results of Aspen-plus based simulation of CO_2 capturing sour compression unit and cryogenic unit. Aspen-plus is then integrated with MS-Excel and MATLAB for databased ensemble learning and sensitivity analysis by SOBOL and FAST method. A discussion of the whole process is held, from CO_2 capturing up to the final storage.

In this study upcoming chapters consists of Literature Review, methodology which states the setting up aspen plus model then next is the results and discussion followed by conclusion.

Chapter 2

Literature Review

Carbon capture can be applied to large-scale emissions processes, including coal and gas-fired power generation, natural gas processing and fertilizer production, as well as the manufacture of industrial materials such as cement, iron and steel and pulp and paper. The application of carbon capture technologies to these processes can play a major role in reducing the world's greenhouse gas emissions. Carbon separation/capture technologies have been operational at large-scale in the natural gas and fertilizer industries for decades and have recently become operational in the power sector.

Energy from fossil fuels such as coal, oil and natural gas is released in the combustion (burning) and conversion process, which also results in the emission of CO_2 as a by-product. In systems where the coal is pulverized to a powder, which makes up the vast majority of coal-based power plants through North America, Europe and China, the CO_2 must be separated at diluted concentrations from the balance of the combustion flue gases. In other systems, such as coal gasification (where coal is converted to chemicals, natural gas or liquids), the CO_2 can be more easily separated.

Fossil fuel-fired cement plants generate a larger percentage of CO_2 emissions than any other industry. Therefore, applying carbon capture technology to that sector – whether on new or existing plants – has the potential for the greatest reduction of CO_2 emissions compared to other sectors. CO_2 capture technologies can be installed into all types of new coal and gas-based plants. However, CCS represents a significant financial investment; appropriate climate policies and regulations that place a penalty on carbon emissions are required to recover these costs and further CCS deployment. The same is true for retrofitting CCS into existing power plants, which requires space and extensive integration to accommodate the CO_2 capture plant

Farla *et al.* (1995) did one of the leading broad investigations on the technological and economic performance of CO_2 capturing from carbon emitting industries [6], mostly for petroleum, iron and steel industry mainly focused on the CO_2 capturing through absorption. It concludes that most of the emissions are from petroleum, while

comparable emissions were from iron and steel. The IEA Greenhouse Gas R&D Program (IEA GHG) has reported intensive findings on the performance evaluation of capturing CO_2 in the 1990s by cement plants and oil refineries [7][8].

Among other Carbon, intensive industries cement is one of the largest Carbon emitting industries. Cement production in 2014 accounted for about 2.2Gt of CO_2 emissions, counting 0.54% and 0.46% of process and heat emissions, respectively [4]. Such high emissions are since the combustion of fuel and decomposition of raw material. Four different cement production methods are wet and semi-wet process, dry and semi-dry process and among these four the dry process is the best available technique [9]. Principal constituents of the raw mix for cement production are calcium carbonate ($CaCO_3$: from limestone), alumina, silica, and laterite. To produce the clinker, temperature around 1400^oC is maintained in the kiln to heat the raw meal, therefore it can be sintered. CO_2 and CaO produced after decomposition of $CaCO_3$ as per (Eq. (1)).

$$\mathbf{CaCO_3 \longrightarrow CaO + CO_2} \qquad \mathbf{(1)}$$

To manufacture cement, the clinker is mixed with performance enhancer additives after cooling and grinding. Specific heat demand of production of cement through the dry process is approximately 2.9-4.6 GJ/t clinker [10]. In such a case, the explicit CO_2 in flue gas emissions estimated around 0.9-1.0 t/t cement (feedstock and energy accumulated) [11]. Owing clinker/cement ratio, the 60 per cent of the aforementioned CO_2 is produced from the process of calcination and the remaining comes from fuel burning. The common demand for the specific electricity is estimated at approximately 0.32-0.54 GJ/tons of cement. In some countries, Refuse Derived Fuels (RDF) are usually incorporated in fuel for cement production. A good example of refused derived fuel usage has been established by ENCI cement plant located in Netherland. In order to promote waste to product and industrial ecology, the plant is utilizing more than 95% of the total fuel in the form of treated biomass along with alternative options such as processed waste and sludge. For a usual kiln size which is round 6000t/d clinker production, the flue gas generally consists of around 15-30% of CO_2 [11].

The European Union's (EU) Strategic Energy Policies 2030 and 2050 set a clear focus for advancement in the contemporary European climate system on low-carbon energy with decreased greenhouse gas (GHG) discharges, rising energy efficiency and a widening portion of renewable energy sources (RES). Especially for 2030 a 40% reduction in CO_2 outflows and a 27% EU-wide green energy commitment for critical energy needs is expected. During the past few years, the average power age mix in the EU has reflected a downturn in fossil commodity age (mostly coal and gas), weakening portion of atomic and dams and a gradually rising share of renewables. There are different paces in the EU Member States' energy shift with Germany and Austria to gradually concentrate on extending the adopted cap and the development of the RES while at the same time other countries are straying from meeting EU goals. With the 21st United Nations Conference on Climate Change in Paris in 2015, COP21 sets another benchmark – restricts average normal temperatures to just below 2°C in order to put together world international responses and environmental change initiatives. From Figure 2.1, it is clear that since pre-modern days, CO_2 and global temperature contradictions have arisen. It supports the initial initiatives and relevant regulations of the EU for lowering carbon emissions and the thermoelectric industry is prepared to deal with the associated difficulties.

The new plants are now run with low parts efficiencies and thus high energy consumption and gaseous emissions. The armada will also not contribute to the policy targets. Around the same time, the extension of RES can not be carried out without assessments of well-being and conscientious consideration. The decrease in the petroleum driven plant cap without countermeasures impairs energy protection because it is almost impossible in an urban environment such as the EU [12].

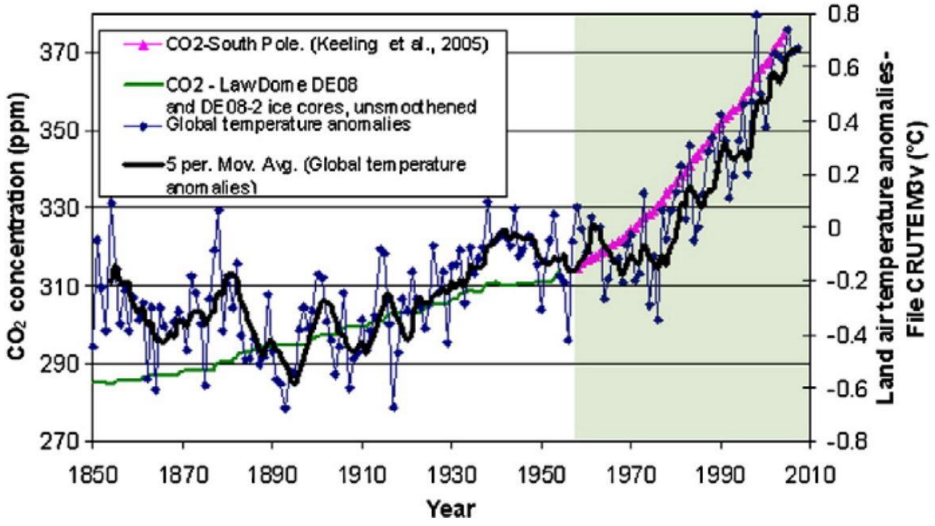

Figure 2.1: Global Temperature irregularity [12].

Several sources of carbon dioxide from where it can be captured as per indicated by its partial pressure, gaseous mixture and working conditions. Reasonably modest separation is allowed by the extended concentrations of CO_2. Hence, as CO_2 is essentially a principal product, it can be extracted or accessible at each stage of burning. In the process of producing energy with the assistance of thermoelectric power, which includes renewable and non-renewable sources of producing energy by the burning process, become the excellent source of producing CO_2, (Post-Combustion Capture-PCC). In general, there are two additional classifications for capture: the fire trap of oxygen-fuel where practically unadulterated oxygen is used in the process of burning CO_2 recycles and pre-combustion trap [13][14].

2.1 Chemical solvent-based CO_2 capturing from post-combustion processes

Among the broader sense of CCS advancements, chemical and physical absorption are viewed as the record near market ways, which are to be implemented at the modern gauge, chiefly centered on their execution in energy manufacture from non-renewable energy sources [15]. On the other hand, Post-combustion capture is an additional important course for seizing less concentrated CO_2 (normally 3–15%) from flue gas and preparation of an unpolluted CO_2 stream (> 99%) for additional modern preparing [16].

2.1.1 Amines based absorption solvents

This capture system is generally known to be the most viable retrofit for conventional power plants because of its limited effect on power plant activity. The technology is equally fine and can be carried out with negligible risks, but the expense of using the breathing gas supply, in general, is restrictively high due to the normally less pressure and CO_2 concentration. New, less expensive solvents should be produced in this power until widespread use [17]. In fact, major investments are made in the following fields:

i. CO_2 kinetics with solvent collection solvents, which reduces the diffusion of solvents and size of equipment.
ii. enthalpy reactions, thus reducing energy needs for regeneration during desorption.
iii. Enhance absorption capacity by reducing solvent circulation rates directly.
iv. Improve thermal stability and oxidative degradation tolerance, the maquillage solvents and additional solvent waste processes.
v. Increase the manufacture of solvents, minimize the overall cost of the activity.
vi. Corrosion reduction, toxicity and risks to safety.

The solvents used for CO_2 processing are classified into firstly clear alkanolamines and alkanolamines that are sterically damaged. Main, secondary and tertiary alkanolamines are found in the basic alkanolamines. As previously mentioned, MEA or DEA will react more rapidly to CO_2 as a result of carbonate formation but with less CO_2 absorption potential as a result of the 1-mole CO_2 reaction process requiring two moles of DEA or MEA. The regenerative capacity needed for high-carbs DEA and MEA solvents is more than that sufficient for MEA.MEA and DEA, particularly MEA, because other gas elements, including oxygen and SOx, occur more likely to undergo oxidative degradation. These often become corrosive, meaning that expensive and costly building materials are required and that capital costs are increased. Nonetheless, MEA typically serves as the natural solvent benchmark for carbon capture and has high importance, both for industrial and academic applications. A number of industrial applications currently use MEA at various levels to test their performance and assess their implementation opportunities (see Table 3).

In fact, this evaluation helps explain the efficiency of new solvents being produced and serves as a benchmark. Also used, as a benchmark for CO_2 recovery is the US Department of Energy (DOE). The recovery of 90% of CO_2 in the gas supply, in order to achieve a high level of CO_2 supply with a purity of 95%, involves an energy recycling of approximately. 4.2 GJ/t CO_2, which leads to an increase of over 85% in electricity costs (COE). The increase in COE suggested that one kWh reduced the price of electricity generation by implementing carbon capture technologies. In fact, most work on new solvents in the United States is planned to reduce COE to less than 35%. [18].

The development of MEA has recently improved via cyclic diamines, especially piperazine (PZ), since PZ has a higher reactivity, higher ability and is resistant to thermal and oxidative degradation [19], [20]. A study group from the Tejas University has studied post-combustion concentrated PZ (40%) and, since 2010, has been used by the URS Group at the National Coal Capture Center (NCCC) on the basis of a pilot-scale of 0.1 MW (Table 3). Results show that PZ concentrate is thermally stable below 150 ° C and that PZ concentrate is 0.3% below 3.0% of the MEA loss when depleted and volatilized at 135 ° C. In this way, the COE rise of 62.6% was noted, which can be further reduced by reducing the cost of producing PZ. Like other amines, however, PZ can react with NO2 in the flue gas and absorb aerosol, resulting in degradation and reduced capacities for absorption [21]. Furthermore, high PZ concentrations can lead to the absorption cycle to precipitation and process instability.

In general, the primary issues need to address as an industrial scale for CO_2 lessening are mentioned below that the amine-based chemical absorption should be addressed [18]:

i. High energy consumption in solvents recycling
ii. Corrosion includes the use of their application of both inhibitors and reactive materials.
iii. Scale-up (800 t/day) from current CO_2 capability to expected (8000 t / day).
iv. O_2, SO_x and other impurities for instance particulates HF, HCl and Hg degradation.

Sterically hindered amines are known as a category of amines, which, relative to standard primary and secondary amines, typically amino alcohols, may increase the absorption rate of CO_2. The amines vary from the production of moderate to low stability carbamates that introduce a large substitution next to the amino group to decrease carbamate stability in the CO_2-amine reaction. Such a weak interaction results in a high free amine concentration within the solution, although the energy requirement for CO_2 release is smaller than the first and second amines. Nicole Hüser *et al*., [21] said the use of obstructed amines could be reduced to as much as 15%.

2.1.2 Non-amine-based solvents

Non-amine solvents are called chemical solvents which do not have an amine cluster in their molecular structure. As a substitute to conventional amine solvents, sodium carbonate (Na_2CO_3) is one of the most effective solvent proposed. Around 30% of sodium carbonate is used in the processing of sodium bicarbonate to provide the necessary atmosphere for the absorption of CO_2 as bicarbonate [21]. The deposition of $NaHCO_3$ increases the production of bicarbonate and thus increases the strength of the solvent's CO_2. The greatest drawback to these solvents is poor absorption. The solvent should be encouraged with the growing amount of additives.

2.1.3 Blends of different solvents

Theoretically, amine mixtures can increase CO_2 uptake to decrease the consistent reboiler duty and the typical circulated solvent volume. Nevertheless, by adding small amounts of tertiaries (MDEAs) to the basic or secondary amine aqueous solutions (MEAs, DEAs) as a solvent mix, the overall solvent behavior is enhanced by the solvent regeneration energy requirements and increased solvent degradation resistance, apart from their reduced reactivity [22]. For the said problem investigators are researching new solvent formulations and mixtures that use strong kinetic solvents like MEA, such as TEA, 2-amino-2-methyl-1 (AMP), benzyl amine (BZA) and MDEA, in other slow-kinetic solvents. As far as CO_2 chemical absorption is concerned, a rising number of carbon capture solvents have been proposed. The first amine to be combined with stronger functional amines was N-methyl diethanolamine (MDEA).

Amines such as amine methanol (MEA), diethanolamine (DEA) and piperazine (PZ) have been used as proprietors of MDEA mixtures. When conjunction with a faster solvent the reaction rate of fast solvents can also be increased. MEA, for example, is a solid solvent, but almost 50 times lighter than PZ. The CO_2 absorption rate of MEA can be significantly improved by adding small amounts of PZ as a booster. The rate of human absorption was increased by this mixture. Potassium carbonate supported by PZ, along with PZ and AMP mixtures, is known to be a good solvent [23].

2.1.4 Ionic Liquids

A modern wave of solvents, including ionic fluids, recently appeared as a substitute to straight amine-based solvents. They are carbon-based salts with high boiling temperatures, hence reduced vapour pressures, and acid gasses such as CO_2 or SO_2 are primarily absorbed where regeneration energy demands are relatively low. Clinton et al. t his problem has been thoroughly discussed recently [24].

Conventional ILs as a liquid solvent interact with CO_2. Despite Henry's action, this increases CO_2 solubility. Functional ILs consist of a group of amino amines which increase CO_2 absorption and the kinetics of main and secondary amines through Zwitterion mechanisms. Scientists are currently engaged in the production of ILs as a possible CCS solution based on their excellent CO_2 capture solvent characteristics. The key property of the ILs is their extremely high potential in certain applications to be synthesized. The tunable solvent characteristic of ILs allows them to provide new molecular structures for developing, in particular, low CO_2 concentrated flue gas [25]. Other properties should also be taken into consideration, including their low vapour density, owing to their effect on the atmosphere. IL's are non-volatile combinations and the concentration of ILs in the cleaning gas is negligible later CO_2 separation [24]. The solvent losses of ILs in the CO_2 capture cycle dependent on these new solvents should be completely avoided. This effect is often correlated with reduced energy consumption as solvents are treated. Several experiments found that the overall energy consumption of the MEA was reduced to 15% by conventional MEA scrubbing [26].

2.2 Physical solvents for CO_2 absorption

It is highly advised that physical absorption mechanisms in pre-combustion systems usually work at high CO_2 partial pressure. In interaction with a gas stream, solid solvents can absorb CO_2 selectively without a chemical reaction. As stated in this introductory section, the physical absorption efficiency can be optimized by high partial CO_2 pressures and low temperatures unit for absorption rate and level of CO_2 solubility. The heavy solvent (CO_2) is consequently regenerated [29]. Seven approaches use actual solvents, such as selexol, rectsol, etc. based on the pre-combustion CO_2 capture process itself are currently commercially available.

Air product and Vattenfall have been working together for capturing of CO_2 from flue gas of coal-fired power plant. Their collaboration focused on the development of a pilot plant for CO_2 recovery with the inclusion of sour compression unit, automatic refrigeration and finally development of membrane for CO_2 separation. So, tests were conducted and results were submitted at the second oxy-fuel conference [27].

For removal of NOx and SOx from flue gases was done by increasing pressure up-to 30bar. At this elevated pressure, NOx/SOx both reacts with water and CO_2 present in the gas stream. So, by controlled formation of acids made saving potential cost and minimizing corrosion of plant. Sour compression and results are very important as combined research by Imperial College London and Schwarze Pumpe leading to the pilot-scale demonstration of this experiment [28], [29]. While CO_2 capturing from flue gasses of cement is under intense research but none of the pilot-scale work has been done so far. So, the usual removal of NOx/SOx is proposed to be different methods which are alkaline scrubber for removal of thermal-based NOx [30], CO_2 cold capture system CRYOCAP designed by Air Liquide [30] acid formation by the SOx and NOx at elevated pressure and then their removal through Lead Chamber process [31][32] and production of sulphuric and nitric acid inactivated CarbonCarbon as adsorbents for SOx/NOx removal [33].

However, the three basic steps for the impurities removal are desulphurization/ denitrification through compression, moisture adsorption through silica or activated carbon-carbon and inert gases separation through flash tanks or distillation unit. Pipitone *et al*., [34] put forward a detailed study on the usage of either distillation

column and flash units. Two different flue gases from natural gas-fired and pulverized fuel-fired power plants were considered. Impact showed on the plant performance and CO_2 recovery. Usage of purified CO_2 for EOR was not feasible by the distillation column as it was unable to reduce oxygen significantly.

For a stable and efficient operation of CO_2 capturing unit with good quality and high productivity, a robust sensing and control system is vital. The databased model also termed as databased virtual sensors have been attracting attention in the process industry for enhancement and replacement of the conventional hardware sensors such as flow meter, pressure gauge and composition analyzer due to the maintenance, accuracy, deterioration and dynamics issues. Kano (2013) mentioned usage of online virtual sensors in process industries and also emphasized on their related issues like (a) change in process/operation condition, (b) difference in any individual equipment and (c) accuracy [35].

Due to the advent of machine learning has been aggregating enormously in recent years because of growing demand and progress in technology. Principal component analysis, partial least square, ensemble learning, and artificial neural network are a few methods used for the development of the database virtual sensor [36]. Broad varieties of machine learning algorithms that are categorized into three groups.

Particularly, the cement industry application of soft sensors is widely studied like Pani A. K. *et al.,* investigated clinker quality produced by rotary kiln by using a back propagated neural network [37]. Similarly, Seraj M. *et al.* used the MLP neural network technique to predict the performance of grate clinker cooler for maximizing heat exchange and heat recovery from hot clinker [38]. Moharana P. K. *et al*. estimated the kiln burning zone temperature by using the Kalman Filter Estimation algorithm [39].

In this study, data-based virtual sensors analysis carried out by ensemble learning method, boosting, for prediction performance of SOx/NOx removal and CO_2 recovery. Ensemble learning aids to improve machine learning for better predictive performance [40]. In this study, a databased virtual sensor is designed to relate process conditions, *i.e*., temperature, pressure and flow rate, *etc*., to the carbon-

capturing capability of SCU. Ensemble learning is used to overcome the variance and overfitting of data. An Aspen Plus based model of the SCU comprising of CO_2 capturing, desulfurization and denitrification processes was developed. To capture the behavior of real-time cement plant operation, the process model was converted to dynamic mode through the interfacing of MATLAB-Excel-Aspen. The data was used to develop the virtual sensors through ensemble learning *i.e.*, Least-Square Boosting.

Chapter 3

Modeling Method

This section delineates about the development of aspen plus based model and then MATLAB algorithms for ensemble learning (Least Square Boost) followed by sensitivity analysis by SOBOL and FAST technique.

3.1 Flow Sheeting

A proposed process flow diagram of cement plant integrated with CO_2 capturing and conversion units is shown in figure 3.1. CO_2 capturing based on the cement plant as shown in figure 3.1 the CO_2 purification unit is integrated with it. Combustion of pulverized coal for clinker production is carried out in the kiln and pre calciner. In clinkerization calcium carbonate disintegrate into calcium oxide and CO_2, this process is called calcination. So, staggering amount of CO_2 emission during combustion and calcination is aimed to capture and purified. All the hot flue gasses leaving preheater and cooler are then used for waste heat recovery and fine grinding of raw material and raw coal. Raw mill is used for the grinding of raw material while coal mill is used for the grinding of raw caol. Sub-bituminous coal is used for the combustion purposes with right amount of moisture, Ash and volatile matters. Hence, temperature is lowered down. Before leaving stacks flue gas is passed through dust collectors outlet flue gases have about 25mg/Nm^3 of dust. Gas conditioning tower is used when additional heat is to be released in open air. Pretreatment and the CO_2 capturing system is employed and integrated with cement plant. Furthermore, this capturing process is divided into three major units: desulphurization/denitrifying (DeSOx / DeNOx), dehydrating and cryogenic units (also called the Sour Compression Unit). In sour compression unit, solvent-based absorption of SOx and NOx takes place. Purification of CO_2 is carried out cryogenically under low temperature and high pressure to liquefy it from remaining flue gasses.

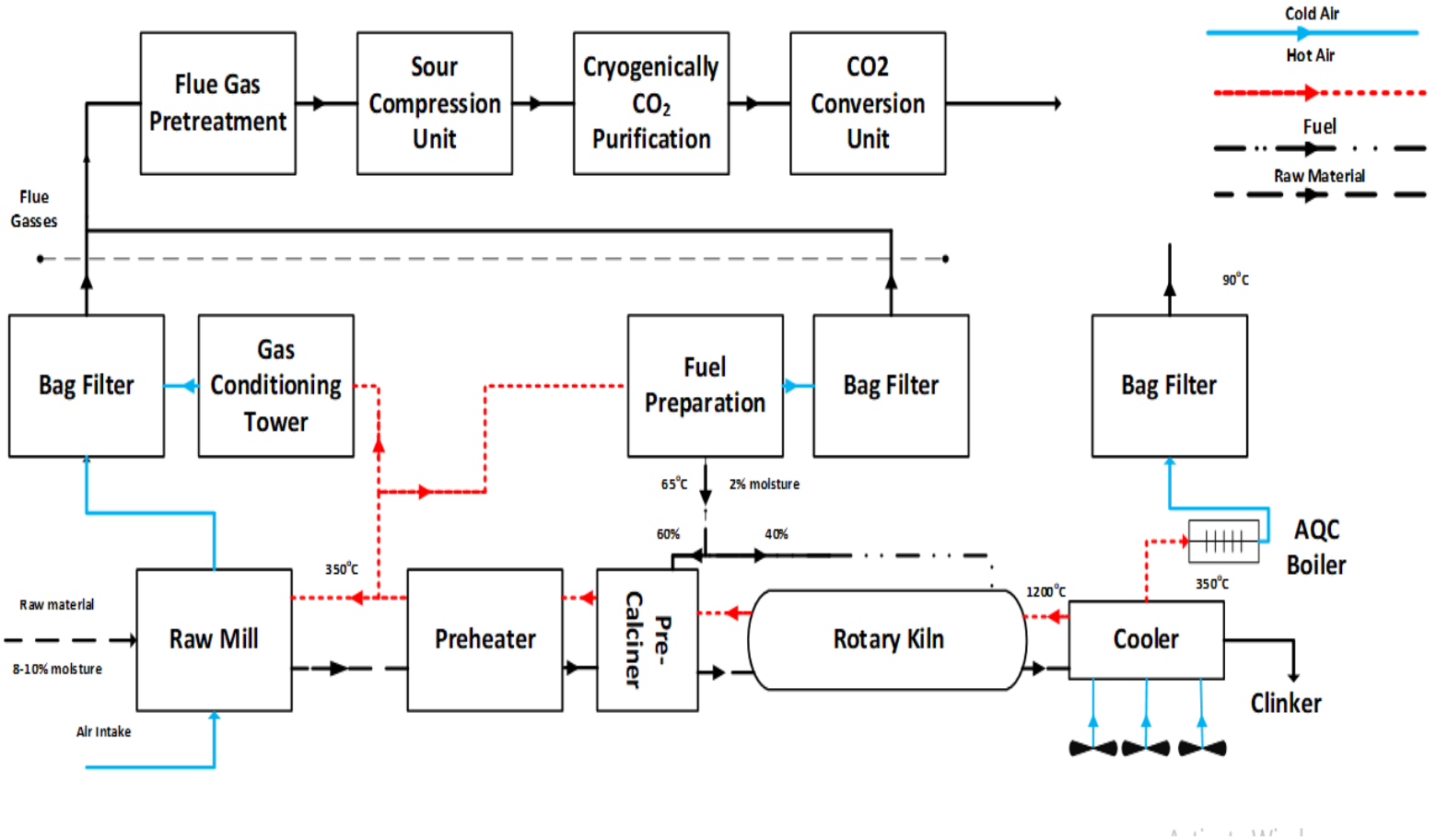

Figure 3.1: Integrated framework for CO_2 capturing and conversion in a cement plant.

3.2 Aspen-Plus Based Process

A Process Flow Diagram (PFD) of SCU developed in Aspen-PLUS is shown in Figure 3.2, [33]. Flue gasses containing N_2, CO_2, O_2, NO, SO_2, and moisture are taken from oxy-fuel cement plant after de-dusting and cooling the slipstream to condense the residual water up to some extent. Then stream passed through a dual-stage compressor with an inter-stage cooler to cool down the heated stream during compression and a flash tank to carry out excessive water. Then it enters into the first absorber counter currently with water to remove SO_2. The gasses then leave from top of the absorber to the third compressor where compression takes place up to 30 bar. Then it enters into the second absorber where NOx is removed by water. These two absorbing towers are with packed material and valid phases are Vapour-Liquid. Removal of SOx and NOx takes place at high pressure up to 30bar. But during the compression process, most of SOx and NOx undergoes chemical reaction for acid formation. As this acid formation has an adverse effect on the process these reactions are then utilized in a specific way so that SOx and NOx can be removed easily. This utilization saves process efficiency and also expected corrosion of equipment. These washed gasses are then passed for dehydration of any residual moisture. After the treatment, process with the flue gas SOx and NOx are present in a very minute amount. From Table 4.1, after the desulfurization and denitrification absorber amount of NO and SO_2 in the gas is present in traces that show about the 99% removal of these two gasses.

Two absorption towers work on 15 bar and 30 bar pressure for the removal of SO_2, NO/NO_2 respectively. The design values of both absorption towers are given in Table 3.1 with associated flowrates of gasses and water used. After the denitrification and de-sulphurization step removal of moisture content is inevitable. Water is absorption at 30bar pressure in the dehydration unit, which is composed of dual bed Temperature Swing Absorption (TSA). Water absorption can take place in activated alumina, silica gel or molecular sieve alumina. If required, a typical regenerative desiccant dryer supply dew point of -40°C to -70°C. Water at the end of SCU is about 0.05 ppm in the gas phase.

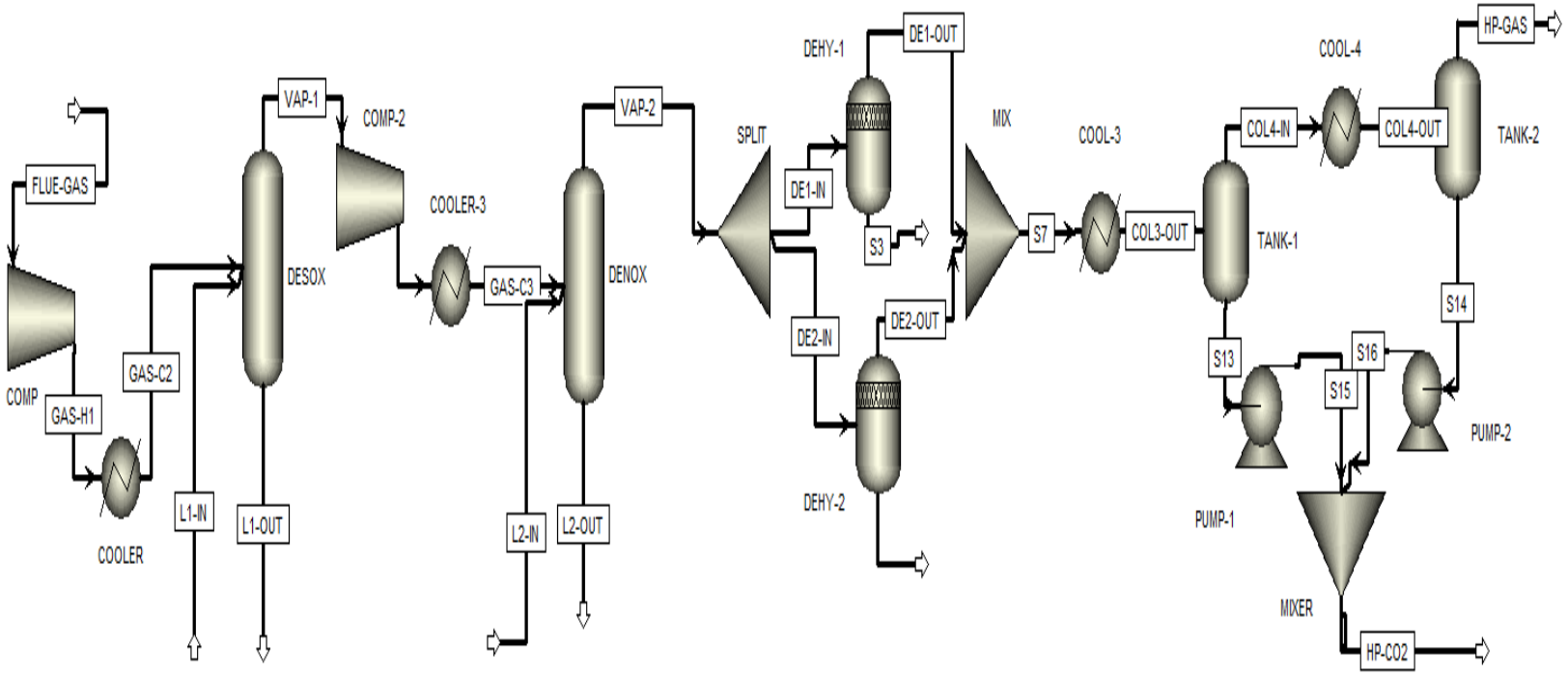

Figure 3.2: Flow diagram of "oxy-fuel cement plant including the CO_2 sour compression unit and cryogenic unit".

Table 3.1: Design Specification of absorption towers.

Design Specification	1st Absorber	2nd Absorber
Calculation type	Equilibrium	Equilibrium
Top stage pressure	16 bar	30 bar
Number of stages	10	10
Flue gas feed stage	10	10
Water feed stage	1 (Top)	1 (Top)
Total liquid flow rate	2339 lb mol/hr	7015 lb mol/hr
Total gases feed rate	7946 cum/h	7873 cum/hr

The dehydration unit gas is cooled (COOLER-3) and flashed at 30bar in the first light (Flash-1). The vapour stream is then cooled (COOLER-4) and then blinked again with the lowest temperature at -53°C in a corresponding flash (Streak 2) so as to keep the dry ice (solid CO_2) away from the structure at this pressure. The second flash vapour stream then passes through a turbine (VENT) which reduces its pressure to 1atm. Streams from both flash tanks shall then be combined and deposited at a pressure of 110 bar. Both Tank-1 and Tank-2 temperatures are very critical and must be controlled for improved cleanliness and recovery. The recovery of molar CO_2 is known as.

$$\text{Recovery of } CO_2 = \frac{molar\ flowrate\ of\ CO2\ at\ the\ exit}{molar\ flowrate\ of\ CO2\ at\ the\ inlet}$$

Where-as molar flow rates are at the inlet and at the exit of cryogenic unit.

3.3 Aspen-Excel-MATLAB interface

The proposed modelling framework is shown in Figure 3.3. 550 data sets are generated through inserting variations in steady-state values of process variables by the interfacing of Aspen Plus, Excel and MATLAB for creating the possible scenarios of streams condition and their resulting output. List of nine process inputs which are temperature, pressure and flow rate of inlet flue gas and liquid inlet into the

absorption towers also the pressure of both flash tanks are used for model development are given in Table 4.3. Generated data is used to develop soft sensors through ensemble learning [41].

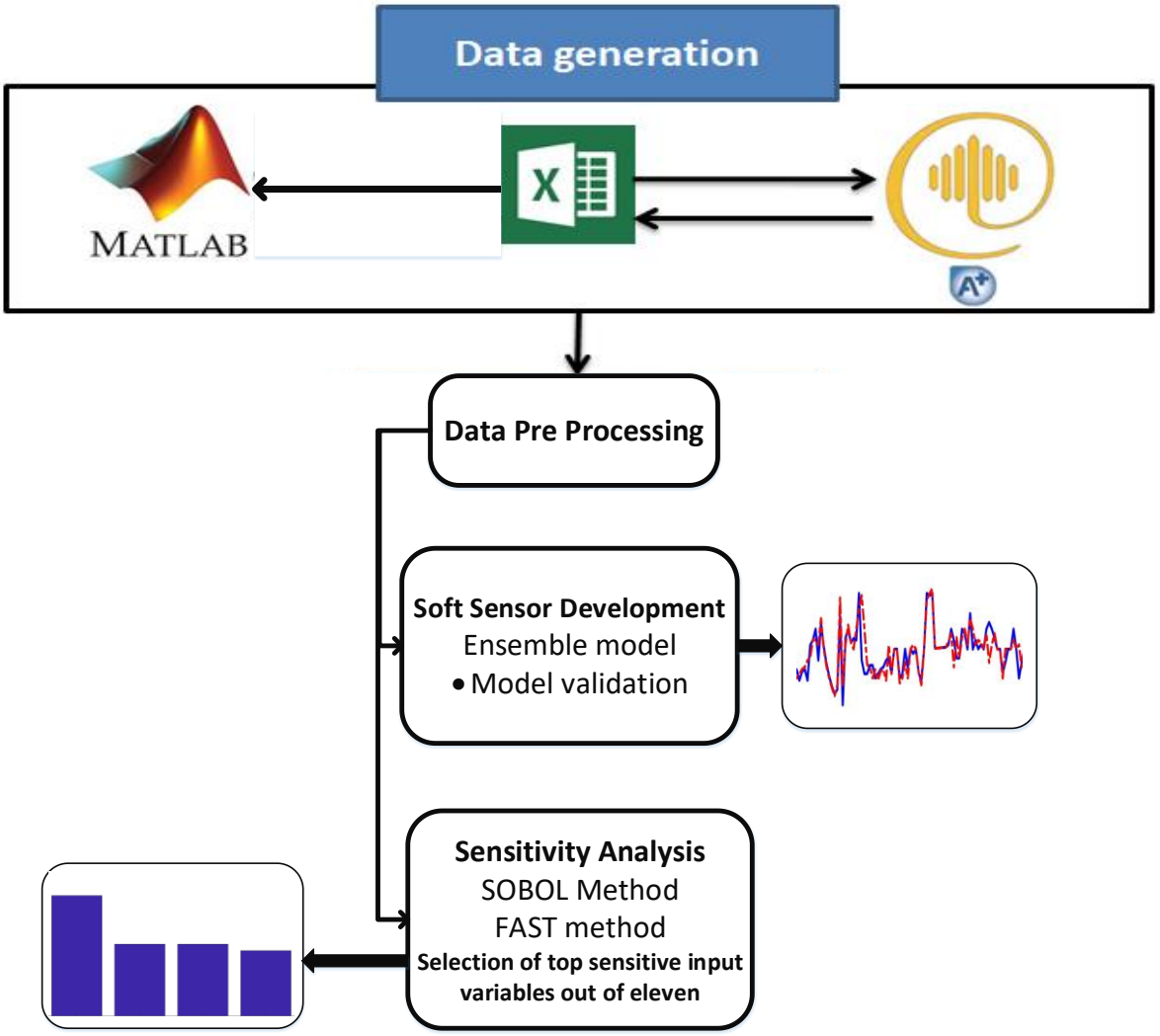

Figure 3.3: Schematic view of data generation.

3.4 Ensemble learning

The adopted technique of ensemble learning, LSBoost, works on the idea of developing a robust model by a combination of several weak models. The concept of developing models of ensemble learning is presented in Figure 3.3. The model is developed in a series of rounds when input is misclassified by a classifier, increases

its weight so that the next classifier is more likely to classify it correctly [42]. Data sets are generated through the interfacing of Aspen Plus-Excel-MATLAB for creating the possible scenarios of streams condition and their resulting output. LS boosting serves as a reality check.

As per Friedman J. H. *et al*., (1999),. the predictive learning problem system consists of a response, variable y, and set of random inputs, variable $x=\{x_1, x_2, x_3,\ldots..x_n\}$. Using the training sample from known response and input set objective is to get an approximation F(x) mapping x-y. That minimizes the expected values some specified function of loss L(y, F(x)) [43].

Here $L(y, F) = (y-F)^2/2$

$F0(x) = \tilde{y}$

For m = 1 to M do:

$\tilde{y}_i = y_i - F_{m-1}(x_i)$, i = 1,N

$(\rho m, am) = \text{argmin}_{a,\rho} \sum_{i=1}^{N} [(\tilde{y}i - \rho h(xi; a)]^2$

$F_m(x) = F_{m-1}(x) + \rho_m h(x;a_m)$

End For

End

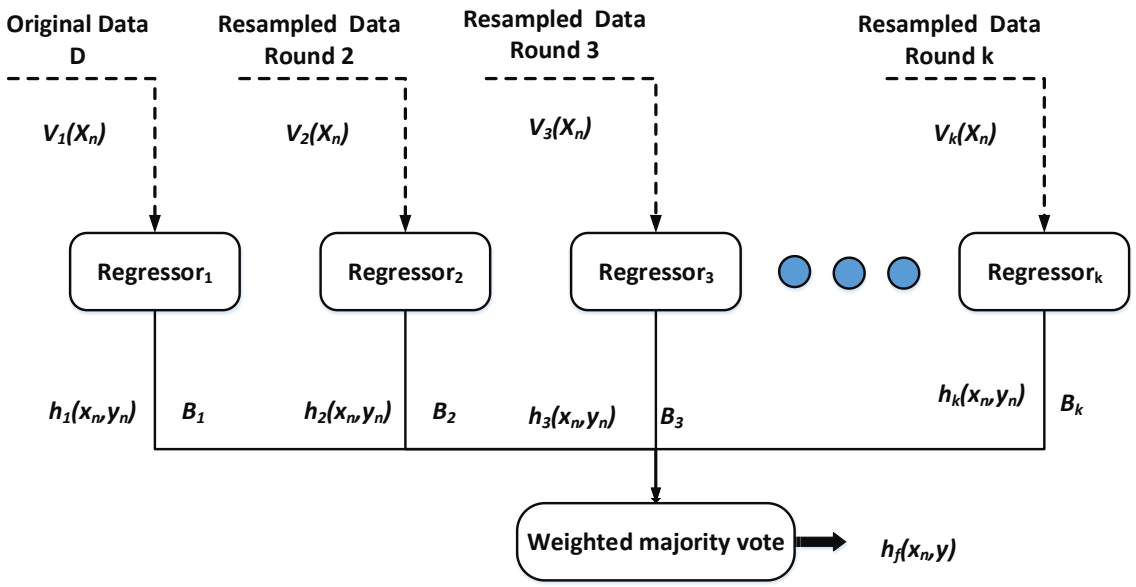

Figure 3.4: Ensemble learning model

3.5 Sensitivity Analysis

The necessity of quantitative and qualitatively understanding of intricate process systems intensifies the use of models to predict sensitivity for certain inputs and outputs. The peculiar mechanism of these models allow for a thorough representation of the underlying network of process outputs and also their response to certain inputs. Sensitivity analysis predicts the influence on output by any input or set of inputs. It provides much information about the input variable which triggers much of variation into the model output [44]. Sensitivity analysis application can be summarized as

a) Understanding input/output relationship
b) Recognizing the imperative and significant model parameters that drive model outputs and
c) Guiding prospect experimentation.

The results of sensitivity analysis help researchers to more focused on the most sensitive and acute parameter that govern model output. Figure 3.4 depicts the steps to follow for data gathering, setting up model, sensitivity analysis and qualification.

Generally, there are two main types of sensitivity analysis which are (i) Local sensitivity analysis and (ii) Global sensitivity analysis.

Local Sensitivity Analysis determines any variations in the output of a model only with respect to single model input. The input variable only changes one at a time with very low increment like 0.1% and the effect of this individual variable on output is calculated by local sensitivity indices. In this analysis, only one variable is responsible for the output also any interaction or relation between input parameters can not be taken into consideration. So, to overcome this problem global sensitivity analysis is used.

Global Sensitivity Analysis: In global sensitivity analysis all of the input variables are varied at a time over whole parameter space, which allows estimating the involvement of each variable and any interaction/relation between them to the model outputs. Input variables have normally wide varieties of variables like temperature, pressure, flow rate, concentration or density. So, this is kind of an advanced approach to determine which process stream having certain behavior constitutes the maximum impact on outputs.

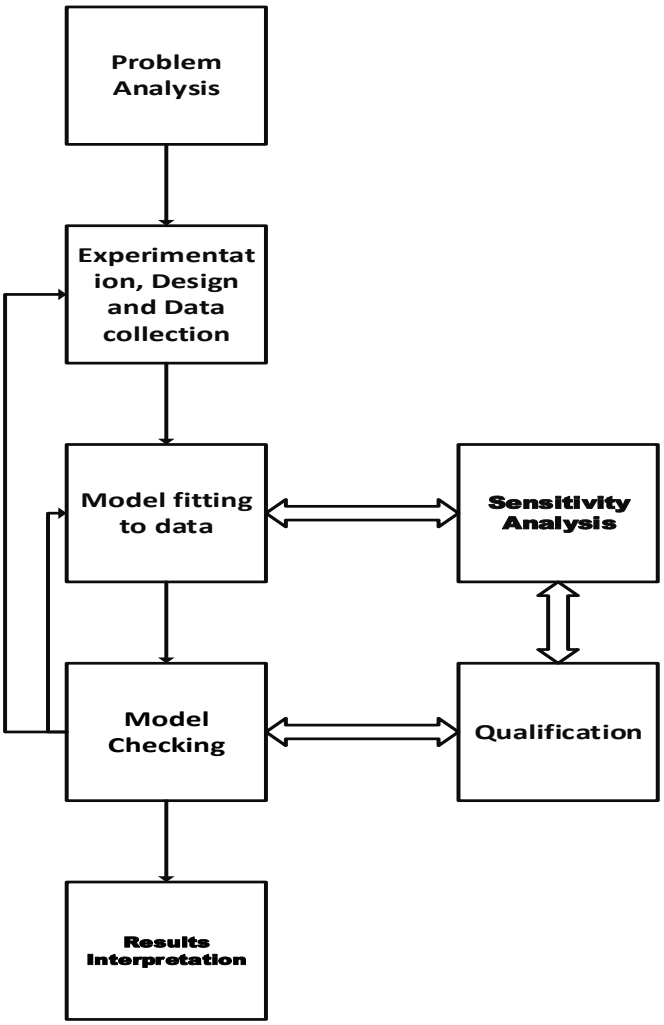

Figure 3.5: Steps for sensitivity analysis and model development

It involves the three-dimensional study of complexity on design, position and process model level. There are other approaches to evaluate multiple model simulation models, reverse parameter modelling methods and sampling-based methods by can uncertainty methods. The main accuracy of study is focused on the SOBOL test methodology and the Fourier Amplitude Accuracy Scale (FAST). Both SOBOL and FAST methods are based on variance decomposition techniques to provide a quantitative contribution of input variables to the output variables. The main difference between SOBOL and FAST is the algorithm based on the integration of indices a Monte Carlo integration is used in the SOBOL while the sinusoidal function is used in the FAST method [45].

3.5.1 SOBOL Sensitivity Analysis

SOBOL check is a variance-based analysis that is named by Ilya M.Sobol, as a SOBOL tool or SOBOL map. SOBOL in a probabilistic context used to determine the effect of the individual input or series of data on the overall model output variance in computational modelling [46]. The input variables in Table 4.2, are evaluated for sensitivity analysis, so they will collectively measure their impact on output. SOBOL doesn't identify what causes the input variability it just identifies the impact on the model output. SOBOL sensitivity analysis has some features listed as follows.

- No supposition(s) between model input and output parameters.
- Evaluation of input parametric variation and interactions between them over the entire space.
- High computation intensity is the main shortcoming.

So, to understand how input variables interact each other to have final output the SOBOL indices can be calculated. For a model $y = f(\boldsymbol{x})$, where y is output linked by a function f to a set of p input factor $\boldsymbol{x}= (x1, x2, \cdots, xp)$. D is the varience f(x) is the random variable and fo is the mean.

$$f\text{o}=\int f(x)dx \tag{1}$$

$$\text{D}=\int f(x)^2\,dx - fo^2 \tag{2}$$

SOBOL method is based on the decomposition of D into contributions from effects of single parameters, combined effect of parameters and this is done by decomposing f(x).

$$f(x) = fo + \sum_{i=1}^{p} f(xi) + \sum_{1\le i<j\le p} fi,j(xi,xj) + \cdots + f1,\ldots p(xi \ldots xp) \tag{3}$$

The decomposition terms are then created as below.

$$fi(xi) = \int f(x) \prod_{k \neq i} dxk - fo \tag{4}$$

$$fi,j(xi,j) = \int f(x) \prod_{k \neq i.j} dxk - fo - fi(xi) - fj(xj) \tag{5}$$

The representation of *f*(x) variance analysis is based on satisfaction of condition.

$$\int fi1, \dots\dots, ip(xi1, \dots\dots, xip)dxk = 0 \; for \; k = i1, \dots, ip. \tag{6}$$

Now by squares on both sides of equation *f*(x) and integration, we get.

$$D = \sum_{i=1}^{k} Di + \sum_{i<j} Dij + \sum_{i<j<l} Dijl + \cdots + D1,2, \dots, k \tag{7}$$

Where $D_{i1,\dots,ip} = \int f^2_{i1,\dots,ip} (x_{i1,\dots,ip}) dx i_1, \dots, x i_p$ is a variance of $fi1, \dots\dots, ip(xi1, \dots\dots, xip)$, termed as partial variance matching to that subgroup of parameters. SOBOL indices can then be deduced as,

$$Si1, \dots., ip = (Di1, \dots., ip)/D \tag{8}$$

Sensitive indices can be then obtained from the above-mentioned equation by dividing it with D. So, Si shows the partial variance with the total variance and indices should sum up to 1.

$$1 = \sum_{i=1}^{k} Si + \sum_{i<j} Sij + \sum_{i<j<l} Sijl + \cdots + S1,2, \dots, k \tag{9}$$

3.5.2 Fourier Amplitude Sensitivity Analysis (FAST)

Fourier Amplitude Sensitivity Analysis (FAST) has been applied successfully in many modelling and non-linear problems, here it is an additional technique used in the present study for sensitivity analysis [32]. The main idea of employing FAST is to convert n-dimensional integral of *f*(x) into one-dimensional integral.

In Fourier series, the function is expressed like.

$$f(x) = \sum_{k1=-\infty}^{\infty} \sum_{k2=-\infty}^{\infty} \dots \sum_{kn=-\infty}^{\infty} C_{k1.k2\dots..kn} e^{j2\pi(k1x1+k2x2+\cdots+knxn)} \qquad (10)$$

With

$$C_{k,k_2\dots..kn} = \int_{I^n} f(x) e^{-j2\pi(k1x1+k2x2+\cdots+knxn)} \qquad (11)$$

By considering the ANOVA decomposition [47], the component $fi1,\dots\dots,ip(xi1,\dots\dots,xip)$ can be stated as Fourier series by taking into the account the elements in above equation *f*(x) with $i_1^{th}\dots..i_p^{th}$ the only non-null indices (i.e $ki_1 \dots Ki_p$).

In that approach the resulted in invariance in the sums of modules of Fourier Coefficients.

$$var\left[f_{i1\dots..ip}\right] = \sum_{ki1=-\infty}^{\infty} \dots. \sum_{kip=-\infty}^{\infty} |C_{ki1\dots..kip}| \qquad (12)$$

As recommended by *Satelli et al. (1999)* a new independent variable "s" is introduced to quantify multi-dimensional integration into single-dimensional integral [48].

$$x_i(s) = \frac{1}{2}\arcsin(\sin(\omega_i s)) \tag{13}$$

Where set $(\omega_i, \ldots, \omega_n)$ is linear independent frequencies.

The output variance of first-order function the ones depending only on input factor *x*i.

$$E[y|xi] = \sum_i C_{ki} \tag{14}$$

And coefficient can be calculated as

$$C_{ki} = \frac{1}{2\pi}\int_{-\pi}^{\pi} f(s)e^{-j2\pi ki\omega is}ds \tag{15}$$

Chapter 4

Results and Discussion

4.1 Analysis of the Aspen model

This section covers the results by Aspen plus simulation and application to the CO_2 capturing accuracy by integrated SCU and cryogenic unit. The reaction kinetics are imlimented as Adjari et al,. (2015) proposed the reaction pathways of nitrogen and Sulphur based compounds, they also determined the pressure level and removal effect of SO_2 in the presence of NOx [49]. The SOx and NOx reactions, given below.

Stoichometery	phase	Reference
$2NO + O_2 \rightarrow 2NO_2$	V	[50]
$2NO_2 \rightarrow N_2O_4$	V	[50]
$N_2O_4 + H2O \rightarrow HNO_3 + HNO_2$	L	[51]
$2HNO_2 \rightarrow NO + NO_2 + H_2O$	L	[52]
$4HNO_2 \rightarrow 2NO + N_2O_4 + 2H_2O$	L	[52]
$SO_3 + H_2O \rightarrow HSO_3$	L	[53]
$2HNO_2 + 2SO_2 + H_2O \rightarrow 2H_2SO_4 + N_2O$	L	[53]
$2HNO_2 + 2H_2SO_3 \rightarrow 2H_2SO_4 + N_2O + H_2O$	L	[53]
$2HNO_2 + SO_2 \rightarrow H_2SO_4 + 2NO$	L	[53]
$2HNO_2 + H_2SO_3 \rightarrow H_2O + H_2SO_4 + 2NO$	L	[53]
$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$	L	[54]

Increased pressure is quite favorable in the process as reaction rate increases to 3rd power at high pressure. No nitric acid formation until all the SO_2 is converted. Aspen-Plus based simulation results are given in Table 4.1, both NOx and SOx are present

only in minute amount after both absorbers. In addition, the results are given by the cryogenic unit as well. Pure CO_2 is available at the end with minor nitrogen and oxygen gas. Eleven-process input variables were selected for ensemble models development by considering flowrate, temperature and pressure of these input variables, see Table 4.3. SCU, electrical energy requirement by compressors and pumps and thermal energy given by coolers is depicted in table 4.4.

Table 4.1: Overall results of the SCU and cryogenic unit.

Gas Composition Mole fraction	Flue gas Inlet	DESOx outlet	DENOx outlet	Cryogenic inlet	HP-Gas outlet	HP-CO_2 outlet
H_2O	2	0.02	0.025	5.58e-06	-	-
CO_2	83.13	0.8294	0.806	0.81066	0.12	0.8337
N_2	11.11	0.1123	0.1233	0.1452	0.69	0.110
O_2	3.66	0.0365	0.0395	0.0451	0.17	0.056
CO	0.03	0.004	0.00044	-	-	-
SO_2	528 ppm	1.3 e^{-04}	0.5e-^{06} (traces)	-	-	-
NO	530 ppm	8.7e^{-04}	0.96e^{-06} (traces)	-	-	-
Total kmol/hr	14770	14602	13188	11330	317	11013

Abatement rates for NOx and SOx from the SCU unit demonstrate the relative removal comparative to inlet concentrations at the inlet and outlet of both absorption columns. Table 4.2 lists the values of elimination from absorption columns and SCU

Table 4.2: Abatement rates of NOx and SOx

Elimination rate %	**De-SOx**	**De-NOx**	**All SCU**
SO2	34	98	98
NO	96	93	98.5

NO2	92	93	98

Table 4.3: Process input variables.

No	Process Variables	Units	Values
1	**Flue Gas Flowrate**	Cum/hr	7946
2	**Flue Gas Temperature**	°C	35
3	**Flue gas Pressure**	Bar	1
4	**L1-IN Flowrate**	Lbmol/hr	2339
5	**L1-IN Temperature**	°C	60
6	**L1-IN Pressure**	psia	250
7	**L2-IN Flowrate**	Lbmol/hr	7015
8	**L2-IN Temperature**	°C	60
9	**L2-IN Pressure**	psia	1000
10	**Tank-1**	°C	-18
11	**Tank-2**	°C	-53

Table4.4: Electrical & Thermal Energy requirements.

Power Type	Operation	Power (kW)	%
Electrical	1 – 16 bar compression	28015	64.80
	16 – 30 bar compression	13808	31.94
	Pump-1	557	1.28
	Pump-2	847	1.95
	Total	43227	100
Thermal	1 – 16 bar cooler (30°C)	-31067 -19686	41.11
	16 – 30 bar cooler (30°C)	-3124	26.09
	COOL-3	-21577	4.14

	COOL-4		28.59
	Total	-75454	100

Parametric study of the cryogenic unit for the influence of both flash tanks and recovery of CO_2 is carried out. The condensing point of this gas is -18°C and the solidifying point is -54°C. Therefore, in that case, Tank-1 temperature should always be lower than the -18°C and Tank-2 temperature must be higher than -54°C to maintain the gas in the liquefied state. To quantify the parametric study Figure 06 shows that, within a given temperature range, at a lower temperature in the flash tanks resulted in increased recovery of CO_2 gas in the final stream. The required CO_2 recovery based on industrial policy and/or laws of the nation. The optimum CO_2 recovery rate in cryogenic units is 82–96% as seen in Figure 4.1 which will lead to a global CO_2 capture rate of 75.8–93.8%. This recovery rate is, however, well in line with that for CO2 capture plants which are usually 85–90 %t post-combustion [48].

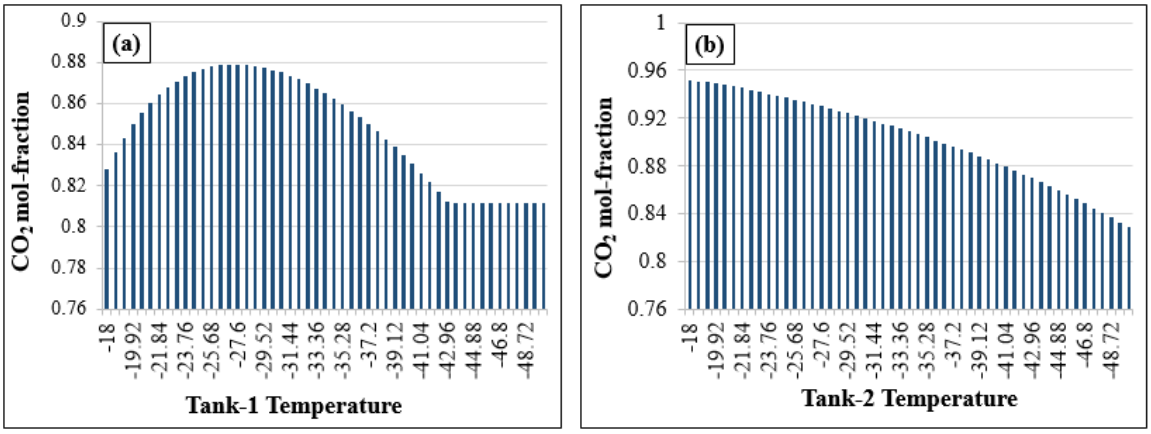

Figure 4.1: The molar fraction of CO2 v/s; (a) 1st flash tank temperature (b) 2nd flash tank temperature.

4.2 Regression Models

A total of 550 datasets containing input and output of the process are generated. 80% of generated dataset is used for model training while 20% of generated dataset is used for model validation. In Figure 4.2 predicted and targeted values are plotted against the test samples of CO_2. Figure 4.3 shows the regression analysis along with the results of

the LSBoost ensemble in terms of the predicted and targeted values of mass fractions of CO_2. Correlation Coefficient and Root Mean Square Error (RMSE) for ensemble model of CO_2 is 0.9888 and 6.5e-03, respectively.

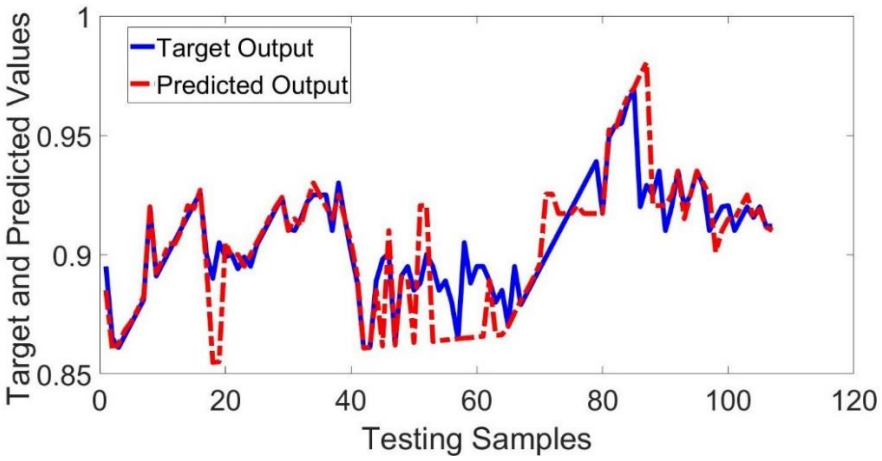

Figure 4.2: Target and Predicted values of CO_2

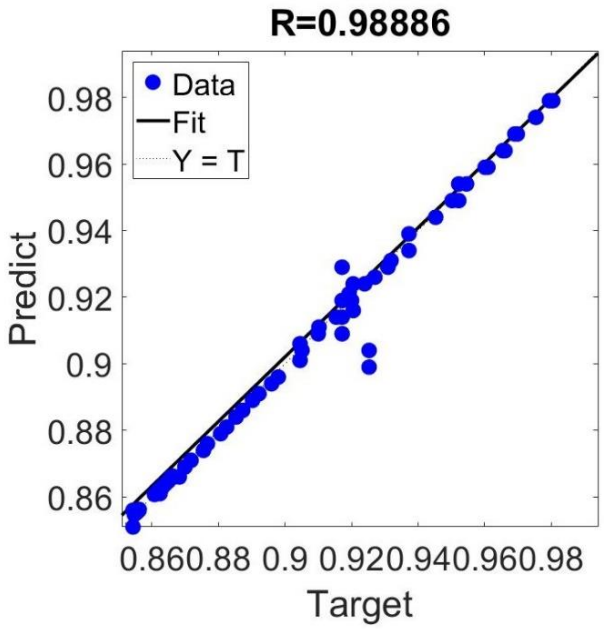

Figure 4.3: Regression performance of ensemble model for prediction of CO_2

In 4.4 predicted and targeted values are plotted against the test samples of SO_2. Figure 4.5 shows the regression analysis along with the results of the LSBoost ensemble in terms of the predicted and targeted values of mass fractions of SO_2. Correlation

Coefficient and RMSE for ensemble model of SO_2 is 0.9663 and 9.95e-05 respectively.

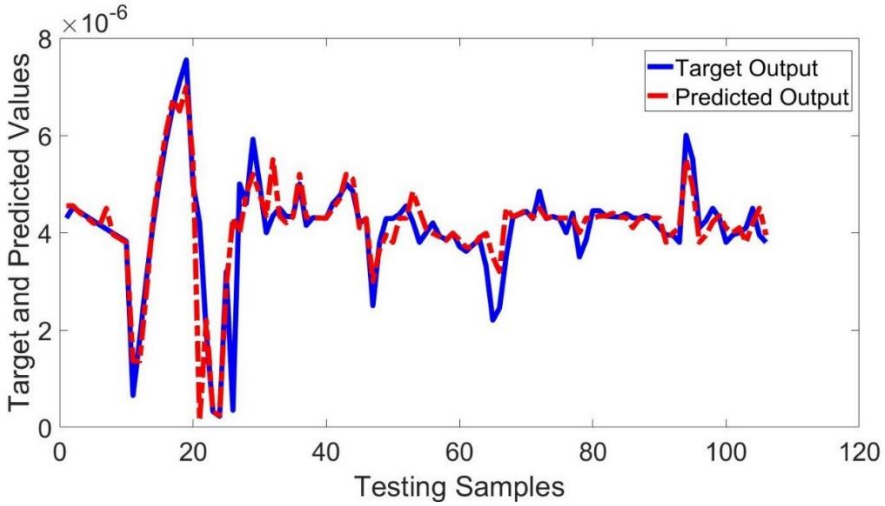

Figure 4.4: Target and Prediction Accuracy of SO_2

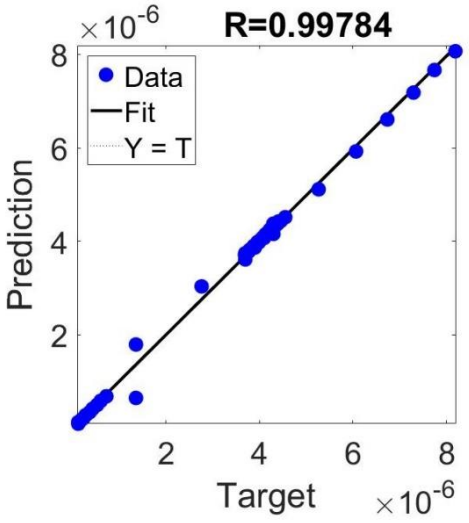

Figure 4.5: Regression performance of ensemble model for prediction of SO_2

In Figure 4.6 predicted and targeted values are plotted against the test samples of NO. Figure 4.7 shows the regression analysis along with the results of the LSBoost ensemble in terms of the predicted and targeted values of mass fractions of NO. Correlation coefficient and RMSE for ensemble model of NO is 0.9970 and 1.03e-06 respectively.

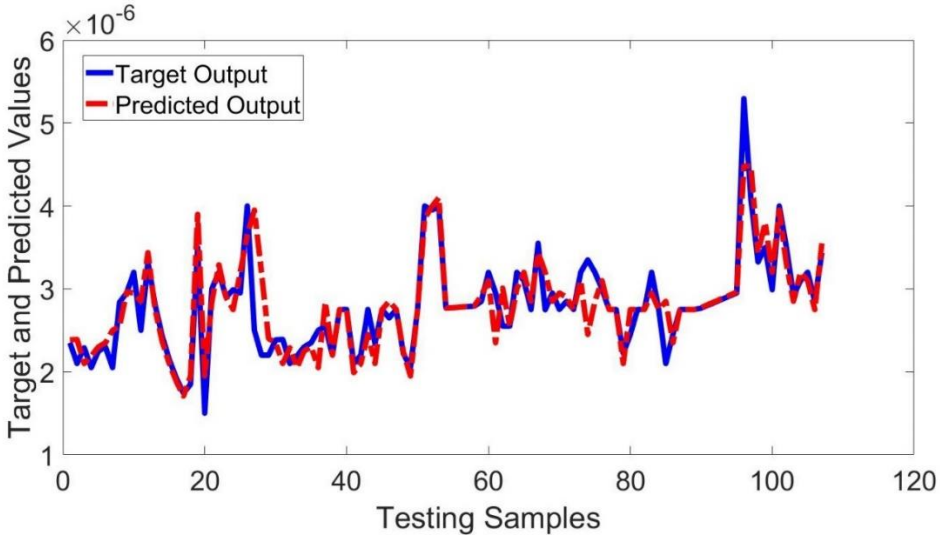

Figure 4.6: Target and predicted values of NO

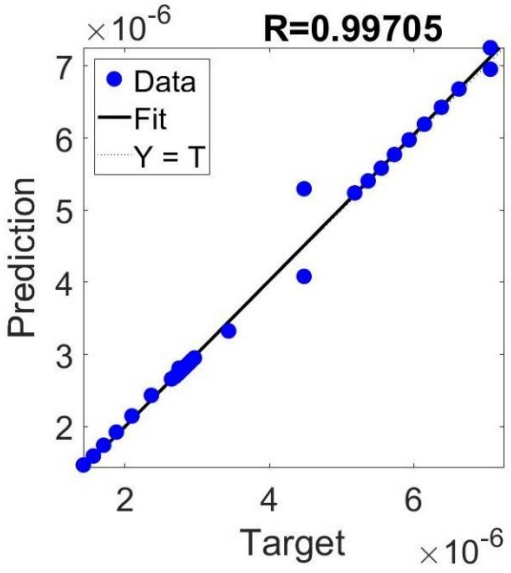

Figure 4.7: Regression performance of ensemble model for prediction of NO

4.3 Sensitivity Analysis

A set of sequences have been established in matlab for computing sensitivity indices by SOBOL and FAST as already mentioned in section 3.5. This is done by generic user-defined model and given the name GSAT (Global Sensitivity Analysis Toolbox). SO, in MATLAB environment the logical flow, as given in figure 4.8, to analyze the sensitivity analysis is to create this new project under name of (*Pro_Create*). Then, by using function of (*Pro_AddInput*) every new variable with its characterstics must be

added. teristics must be added to the project by using the function (*pro_AddInput*). This function requires the name of the variable and a handle to its probability density function (*pdf*) which allows the (*fnc_SampleInputs*) routine to know how to sample the input variables. Two *pdf's* are already implemented: the uniform in an interval and the Sobol' one for the Sobol' quasi-random distribution. Once the set of input variables is defined, the analysis needs an initialization step by the command (*GSA_Init*). In the routine *GSA_Init* the model is, then, evaluated on the points of the first set and the results are stored to be used in the sensitivity computation. After the problem definition and algorithm initialization it is possible to calculate the sensitivity indices.

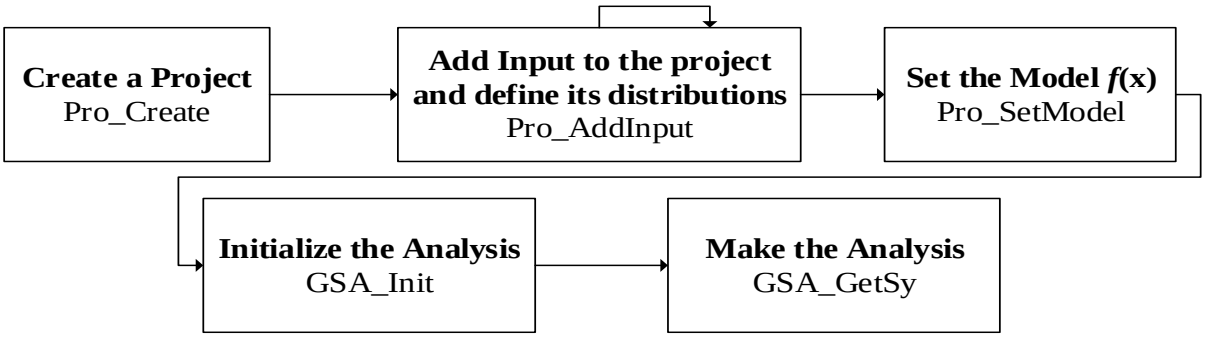

Figure 4.8: Steps to proceed for sensitivity analysis through GSAT

Sensitivity analysis is carried out for removal of SO_2 and NO from sour compression unit and recovery of CO_2 in cryogenic unit. Sensitivity analysis is performed by SOBOL and FAST methods on input process variables given in Table 4.3. Total eleven input variables are used which are temperature, pressure and flow rate of inlet flue gas, also temperature, pressure and flow rate of inlet water of both absorption towers of SCU and temperature of both flash tanks of cryogenic unit.

Sensitivity indices of SOBOL and FAST for the recovery process of CO_2 are shown in 4.9. Temperature of Tank-1 and Tank-2 of the cryogenic unit are found the most sensitive variables. The temperature of both flash tanks is crucial for the recovery of CO_2. However, pressure and flow rate of inlet flue gas and water has no effect on the recovery of CO_2. In order to get maximum CO_2 recovered in the cryogenic unit these temperatures need to be monitored closely. The reason of sensitivity of these two

temperatures can be validated from literature. Meunier et al. (2014) investigated the parametric behavior of flash tanks temperature and concluded about targeted objectives of recovered CO_2 recovery and purity as per international standards [55], [56].

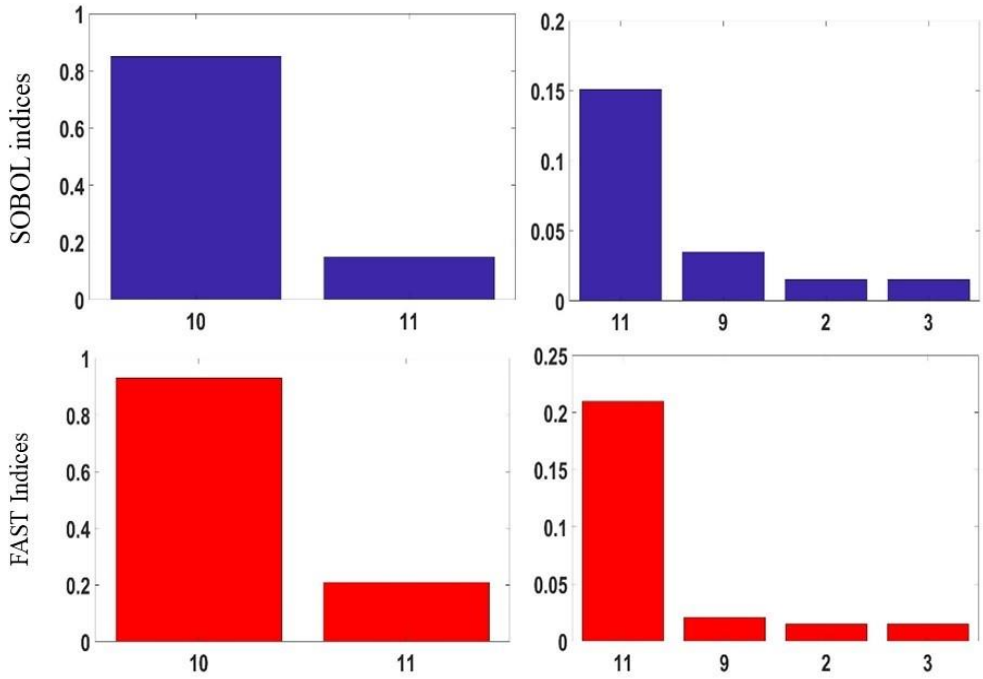

Figure 4.9: SOBOL and FAST sensitivity indices of CO_2

Similarly, sensitivity indices of SOBOL and FAST for removal of SO_2 and NO are given in 4.10 and 4.11 respectively. The trend in both figures depicts that the most sensitive variables are inlet flue gas pressure (second variable) and inlet flue gas flow rate (third variable). Whereas the flue gas temperature, inlet water temperature and pressure at scrubbing towers and flash tanks temperature have relatively less impact on SO_2 and NO removal efficiency. Thomas et al.(1999) performed extensive experiments on efficiency of NOx absorption by water and sodium hydroxide solution in packed column at varied pressure and flow rate conditions of flue gas and it was concluded that high absorption efficiency observed at increased flow rate and partial pressure of flue gas [57]. Pressure and flow rate of flue gas effects the compression in SCU, this compression process in turn affects the flow rate of gases at the inlet of both scrubbing

units. Any change in flow rate of gases at the inlet of scrubbing unit will result in changed concentration of SO_2 and NO.

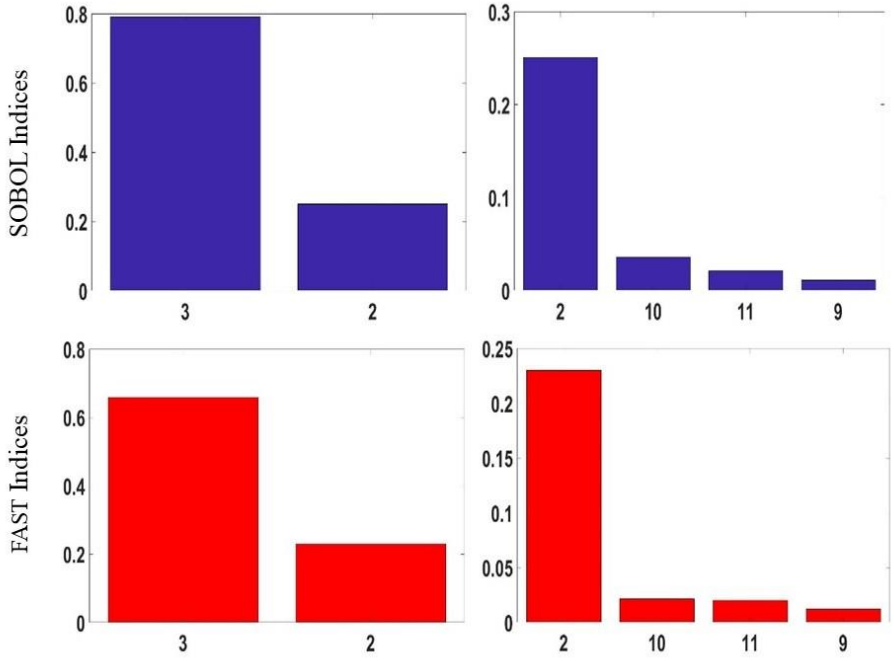

Figure 4.10: SOBOL and FAST sensitivity indices of SO_2

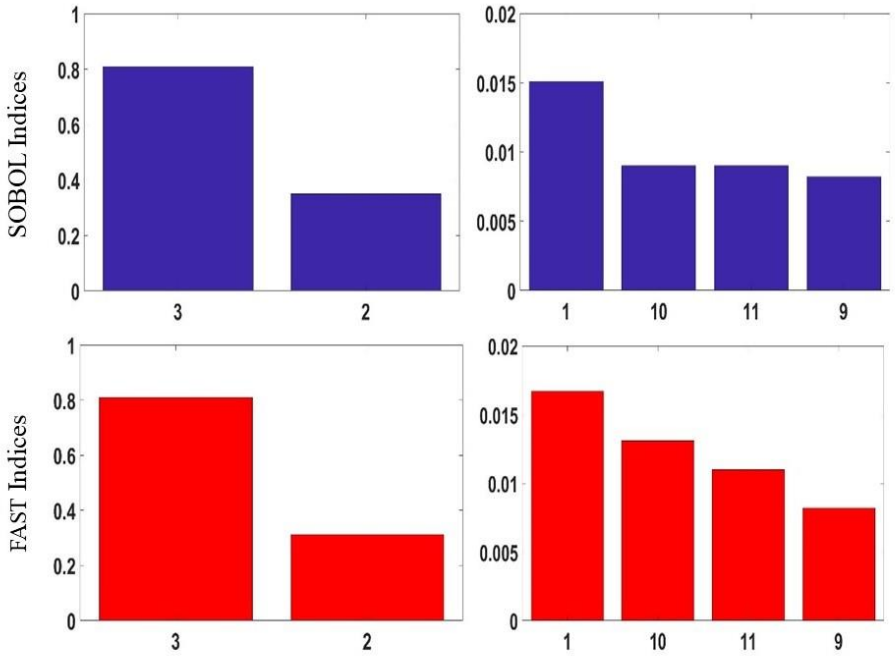

Figure 4.11: SOBOL and FAST sensitivity indices of NO

Conclusion

In this study, Aspen-PLUS based model of sour compression and the cryogenic unit is developed for the analysis of CO_2 capturing. The thermal and electrical energy needed for cooling and compression is investigated. The abatement rates of NOx and SOx from SCU are calculated, along with the recovery rate of CO_2 from the cryogenic unit. A parametric study of cryogenic unit recovery of CO_2 up to 99% depends upon the temperature of 1^{st} and 2^{nd} flash tanks that should be between -18°C to -54°C, respectively. A parametric study for Temperature and pressure dependence of both flash tanks in the cryogenic unit is carried out. For soft sensor development, Least Squares Boosting, a kind of ensemble learning technique, is used. The Sour Compression unit was simulated in the Aspen-Plus environment, and its data generated by interfacing Excel and MATLAB for soft sensor analysis. The soft sensor incorporation through MATLAB with Aspen-PLUS data indicated the high accuracy of the model developed. Correlation coefficients and root mean square error indicated the high prediction accuracy of soft sensors. The accuracy of boosting results of SO_2 and NO removal is 99.6% and 99.7%, respectively, while CO_2 recovery from the SCU unit is 98.9%. As per SOBOL and FAST sensitivity analysis, inlet flue gas temperature and pressure are the most sensitive variables.

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