Indian Institute of Science Sulfur Extraction Technology ISET (Process)

1. Introduction:

Industrialization and urbanization of the society in the present world has increased the levels of pollution in all the three sectors, land, air and water due to the wastes generated. Proper treatment and disposal of the same in order to prevent the damage to the natural resources and the environment is being recognized and pursued at various degrees of seriousness around the world. Different methods are in vogue depending on the type of waste, whether it is biodegradable or non-biodegradable. One of the most common and effective way of treating the biodegradable matter is anaerobic digestion and is infact part of most of the distillery effluent treatment plants and sewage treatment plants. Biogas the product of anaerobic digestion is a mixture of Methane, Carbon dioxide and Hydrogen sulfide. The composition of biogas is mainly Methane, CH_4 (55-65 %), Carbon dioxide, CO_2, (30 - 40 %) and hydrogen sulfide, H_2S, (0 - 6 %) depending on the type of waste and the temperature of the digester used. The calorific value of biogas is around 24 – 28 MJ/ m^3 (depending on the CH_4 content in the gas) and is a potential and efficient fuel source for power generation using IC engines, if the hydrogen sulfide is removed from it.

Need for Hydrogen Sulphide Removal:

Hydrogen sulphide is a highly toxic and corrosive gas and is a major pollutant in fossil fuel based industries, sulphur based chemical Industries and biogas based units and is characterized by the 'rotten egg' smell at low concentrations. Sweetening of biogas is essential because of its toxicity which affects the environment and the highly corrosive nature which corrodes the metallic parts like boiler tubes, engines coming in contact with it in few hundred hours of operation.

Hydrogen sulphide is immediately lethal to humans at 1 - 3 mg/lt of air and causes illness at lower levels. It is more poisonous than hydrogen cyanide. At high concentrations it will lead to almost instantaneous poisoning and death due to the result of complete arrest of respiration. A person over come by this gas should promptly be removed from the contaminated area and given immediate artificial respiration. Exposure to lesser concentrations may result in nausea, stomach distress, belching and coughing. Moderate concentrations may result in eye irritation. Hypersensitivity to H_2S, once established, may remain for a long time.

Impact of Toxicity Levels in Human Woking Envornment:

1.2–2.8 mg/l air (immediately lethal)[1]

0.6 mg/l air (exposure for 0.5–1 h, lethal)[1]

0.1-0.15 mg/l air (a few hours of inhalation, poisonous)[1]

IC engine application requires H_2S concentration to be less than 1000 ppm for satisfactory operation, but lower level of the H_2S would lead to longer life of the system components and also enhanced period fore replacement of the lubricants.

2. Process Principle:

ISET process developed by ABETS, IISc is based on the red-ox reaction of chelated polyvalent metal ion. In this particular process iron in aqueous medium, which exists in both Fe^{3+} and Fe^{2+} form, is used for scrubbing hydrogen sulfide from the biogas. The sulfur present in the hydrogen sulfide is precipitated as elemental sulfur.

3. Process Chemistry:

H_2S when dissolved in aqueous medium is ionized to H^+ and S^{2-}. The sulphur ions can be oxidized by polyvalent metal ions such as those of iron, which can exist in both ferric (Fe^{3+}) and ferrous (Fe^{2+}) state. When the sulphur ion comes in contact with ferric ion complex, it gets oxidized to elemental sulphur and is precipitated.

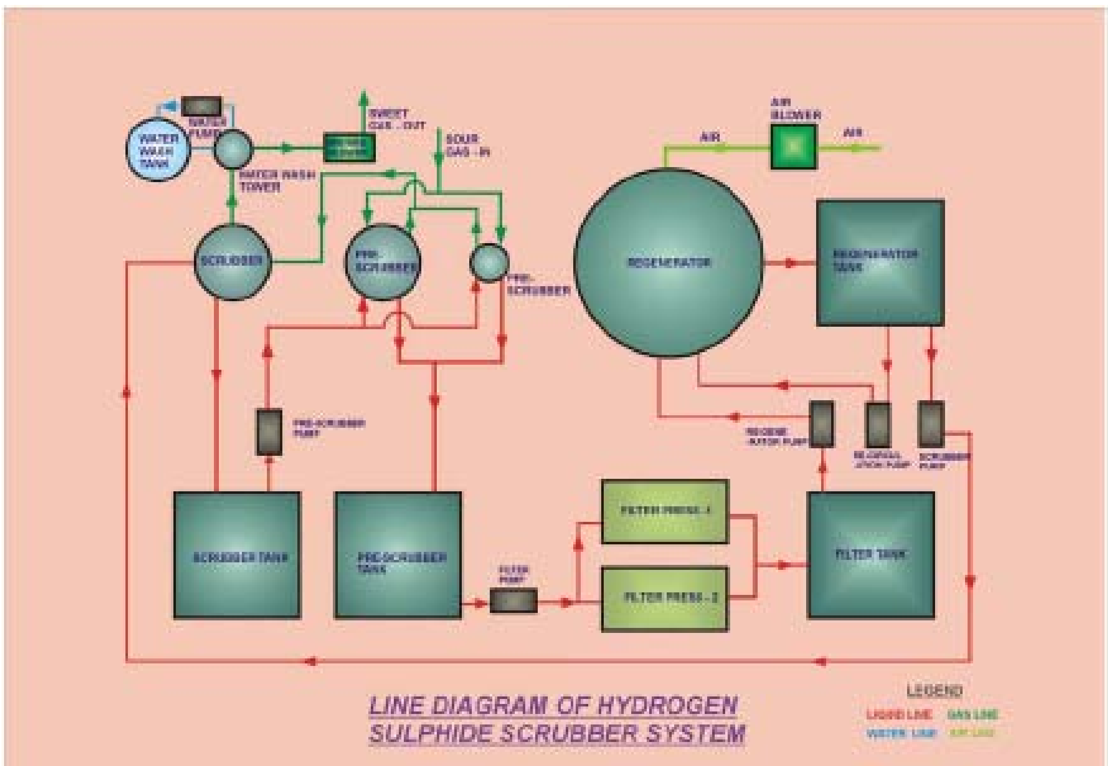
$$2Fe^{3+} + S^{2-} \longrightarrow 2Fe^{2+} + S$$

The ferrous ions are later oxidized to ferric ions by reaction with oxygen in the atmospheric air.

$$4Fe^{2+} + 4H^{+} + O_2 \longrightarrow 4Fe^{3+} + 2H_2O$$

4. Process Description:

The process uses the counter current gas liquid contacting with the gas being taken from the bottom of the packed scrubber column and the scrubbed liquid is pumped form the top in a two stage scrubbing operation. The gas coming out of the scrubber column, which is free of hydrogen sulfide, is then scrubbed with water for cleaning any minute quantities of chemical carried over. The clean gas thus obtained is fit for the end application. The scrubbed solution containing sulfur is then passed through filter press for sulfur removal. The clear filtrate is then regenerated in a coutercurrent with air in a packed re-generation column.



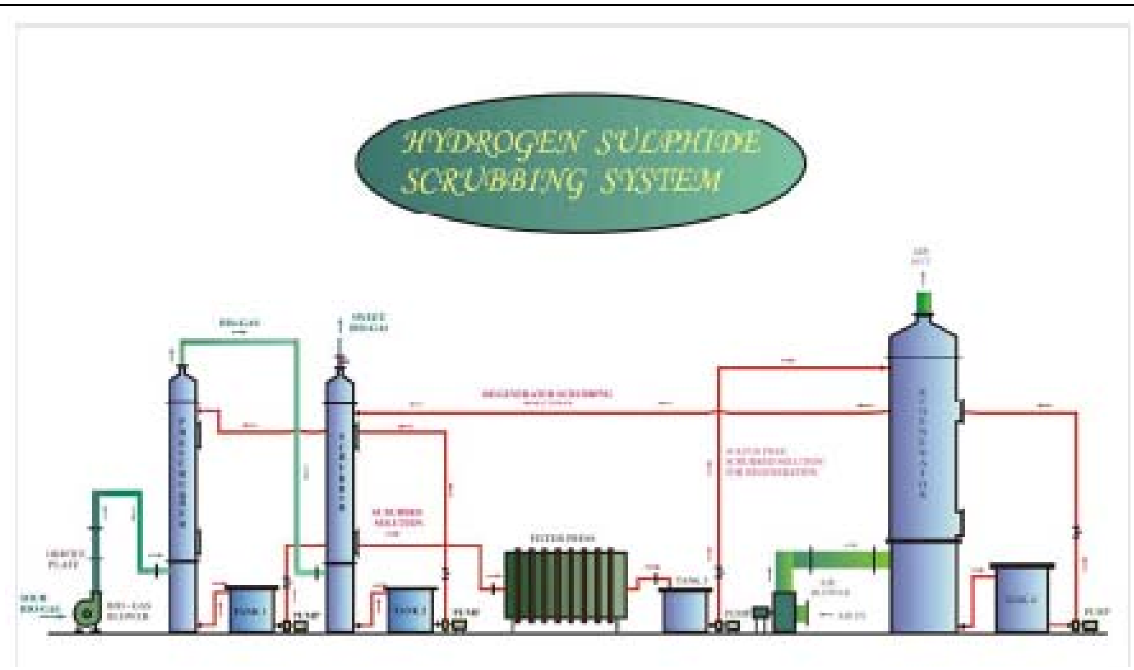
5. The System and its major elements:

- **a. Scrubber**
- **b. Pre scrubber**
- **c. Regeneration tower**
- **d. Filter press**
- **e. Wash tower**
- **f. Biogas blower**
- **g. Air blower**
- **h. Pumps**

a. Scrubber:

In this element, the gas cleaning operation is performed. The tower is packed with Raschig rings to ensure better contact between liquid and gas. A mist eliminator fitted at the top eliminates any liquid carry over by the gas. The material of construction of the column is either concrete with epoxy coating or PP lined FRP and is packed with PP Raschig rings.

b. Pre scrubber:
This element is similar to the scrubber. The difference is that it is packed tower with larger size Raschig rings. The raw gas enters this tower first and then enters the packed tower. Hence it minimizes the blockage of rings in the scrubber due to sulphur deposition. The material of construction of the unit is either concrete with epoxy coating or PP lined FRP and is packed with PP Raschig rings.
c. Regeneration tower:
In this element, the regeneration of the scrubbing solution occurs. This tower is packed with Raschig rings to ensure good contact between air and liquid for maximum regeneration and this also takes care of the cooling of the scrubbed solution. A mist eliminator fitted at the top eliminates any liquid carry over by air. Liquid is injected from top and air is either blown in from the bottom or sucked from the top through the louvers. The column is constructed either of concrete coated with epoxy or PP lined FRP depending upon the volume of gas and the hydrogen sulfide present and is packed with PP Raschig rings.
d. Filter Press:
It is the sulphur separation stage. Sulphur precipitated during the cleaning process is filtered in the plate and frame filter press. The plates are polypropylene recessed plates over which filter cloth, which is also polypropylene, is put. The liquid with sulphur is passed through the plates and it gets filtered as it passes through the cloth. The sulphur is washed and later removed.
e. Wash tower:
The scrubbed gas is cleaned of any minute quantity of scrubbing solution carried over by counter current contact of gas with water. The clean gas goes out of the unit after passing through the mist eliminator at the top. The tower is constructed of either concrete with epoxy coating or PP lined FRP and is packed with PP Raschig rings.
f. Biogas Blower:
Biogas blower installed at the outlet of the scrubbed gas functions in maintaining the required gas flow rate and taking care of the pressure drop across the scrubber elements. This is made of MS with epoxy coating.
g. Air Blower:
This is a component, which delivers the required airflow rate and pressure to the Regeneration Column for oxidizing the ferrous ion. This is made of MS with epoxy coating.
h. Pumps:
The pumps installed at various stages maintain the liquid flow rate across the different system elements. All parts coming in contact with the scrubbing solution are PP lined.



6. Advantages of this process:

- H_2S is converted to solid Sulfur, which has commercial value.
- No gaseous emission
- Low H_2S content in the cleaned gas (< 100 ppm v/v basis) irrespective of the inlet hydrogen Sulphide concentration.
- The system is capable of handling fluctuations in H_2S concentration and biogas flow rate.
- This process is highly selective for H_2S with little H_2S being removed.
- The system operates ambient temperature and pressure.
- Easy start up and shut down.
- Online removal of sulphur generated prevents choking/clogging of regenerator.
- The chemical used is regenerated implying low running costs compared to other systems.
- Tailor made for individual gas flow rates and inlet hydrogen sulfide concentration.

7. Sulfur Quality and its utility:

Contamination of sulfur by the gas will be minimum. Any contaminant by cleaning solution will be soluble in water and hence may be removed by washing with water. The sulfur particle produced in the process is typically 2 – 8 microns and a purity of more than 99 % is achieved. Sulfur for its good vulcanizing property is used in the rubber manufacture. The industrial grade of sulfur finds applications in paper and pulp, mining, steel, and oil refining. Sulfur is formulated for use as nutrients, soil amendments and pesticides. It can also be used in fungicide formulation and finds major application in pharmaceutical industries. This is also employed in sugar industries, petroleum refining and explosives.

8. Utility and Chemical requirements:

i. **Electricity:** The connected electrical power for the pumps, blower and the filter will be about 8 to 10 % of the power generated

ii. **Cooling:** Any cooling requirement is taken care in the regeneration step itself.

iii. **Process water:** Process water for filter cake washing will be about 2 – 3 m^3/ton of sulfur extracted.

9. Process control and operator requirements:

The control system depends on the level of automation required. Intrinsically simple controls and minimal operator attention are sufficient.

10. Cost of electricity produced:

The scrubbing chemicals are regenerated and only the make up chemical has to be added, thus making the process an economical one. The chemical cost of the system is dependent on the hydrogen sulphide concentration in the sour gas. At 3 % hydrogen sulphide concentration the total operating cost is around **Rs. 0.75 - 95/kWh**

11. Maintenance requirements:

Maintenance requirements are minimum in this system as the sulfur suspended in the absorption column and the storage tank is filtered online.

Users and Performance of ISET Scrubbers:

ISET scrubbers have been in operation for the last 6 years at different industries with highly satisfactory results. The following gives the list of installations.

Sl. No	Location	Type of User	Design Capacity	Status
1	UP Jal Nigam, Kanpur	STP	900 m^3/hr 3 % H_2S 1.6 MWe	Commissioned in June 99.Running for 6 – 8 hrs a day H_2S in Sweet Gas < 10 ppm
2	UP Jal Nigam, Allahabad	STP	600 m^3/hr 3 % H_2S 1.1 MWe	Commissioned in June 99.Running for 4 - 6 hrs a day H_2S in Sweet Gas < 10 ppm.
3	KCPSIC Ltd, Vuyyuru, Andhra Pradesh	ETP	600 m^3/hr 7.5 % H_2S 1.0 MWe	Commissioned in 2001 - 2002. 2.0 million kWh generated H_2S in Sweet Gas < 50 ppm
4	USWL, Ugar Khurd, Belgaum, Karnataka	ETP	600 m^3/hr 7.5 % H_2S 1.0 MWe	Commissioned in 2000. 5.0million kWh generated H_2S in Sweet Gas < 50 ppm
5	VISHTEC, Melvisharam Ranipet, Tamilnadu	Leather fleshings	13.5 m^3/hr 3.0 % H_2S 30 kWe	Commissioned in 2000. Running for 6 hrs a day. H_2S in Sweet Gas < 10 ppm

ISET scrubbers are operated on a continuous mode in the Distillery Effluent Treatment Plants (24 hours a day, 7 days a week and round the year) and for period of around 6 – 8 hrs at STP's depending on the gas availability. The operating cost varies depending on hydrogen sulfide percentage and gas flow rate. Typically the operating cost is around Rs. 0.75 to Rs. 95 per kWh at the Indian conditions for inlet hydrogen sulfide concentration of 3 % and gas scrubbing capacity equivalent to 1 MWe.

Fig 1. ISET Scrubber at KCPSIC Limited, Vuyyuru, Krishna District, Andhra Pradesh, India – for Biogas from Distillery Effluent Treatment Plant

Fig 2. ISET Scrubber at UP Jal Nigam, Jajmau, Kanpur, India – for Biogas from Sewage Treatment Plant

Fig 3. Scrubbing Solution used & Precipitated Sulphur produced by ISET Process

ISET Scrubber Performance:
Performance of *ISET* Scrubbers has been good at all the sites where it has been installed. The following graphs shows the data from two locations where ISET scrubbers are in operation on 24 hrs per day, 7 days a week and round the year. The outlet hydrogen sulfide concentration as can be seen from the graph is less than 10 ppm in general and in specific less than 2 ppm at 75 % of designed gas loading capacity. Though the scrubbers have been in operation continuously through out the year, the amount of gas scrubbed and power generated is only around 35 – 40 % of the designed capacity on an average because of the limitation in gas production capacity at the source or power evacuation after production.

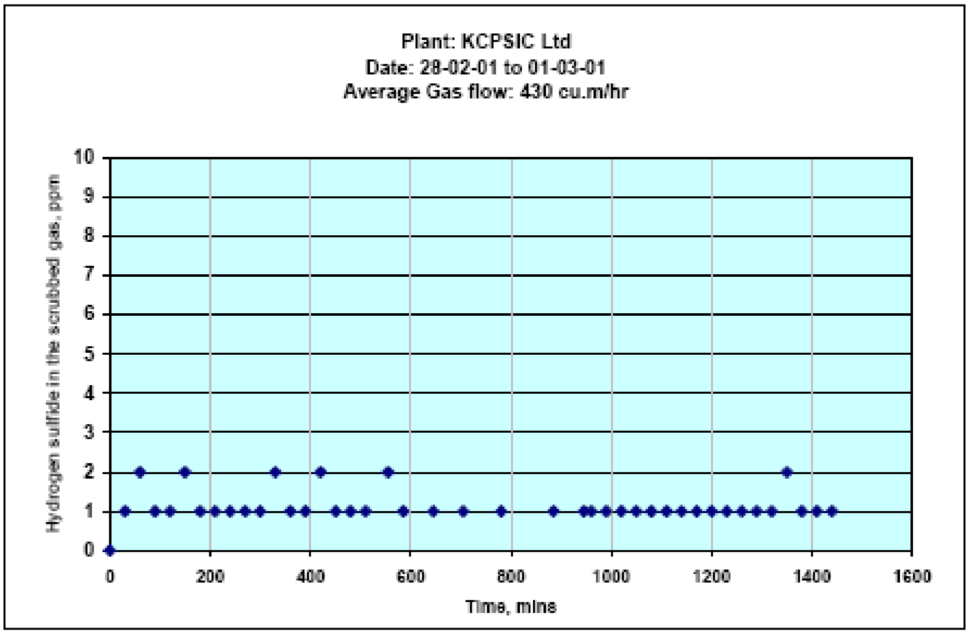


Fig 4. Performance of the hydrogen sulphide scrubbing system at average gas flow rate of 430 m^3/hr

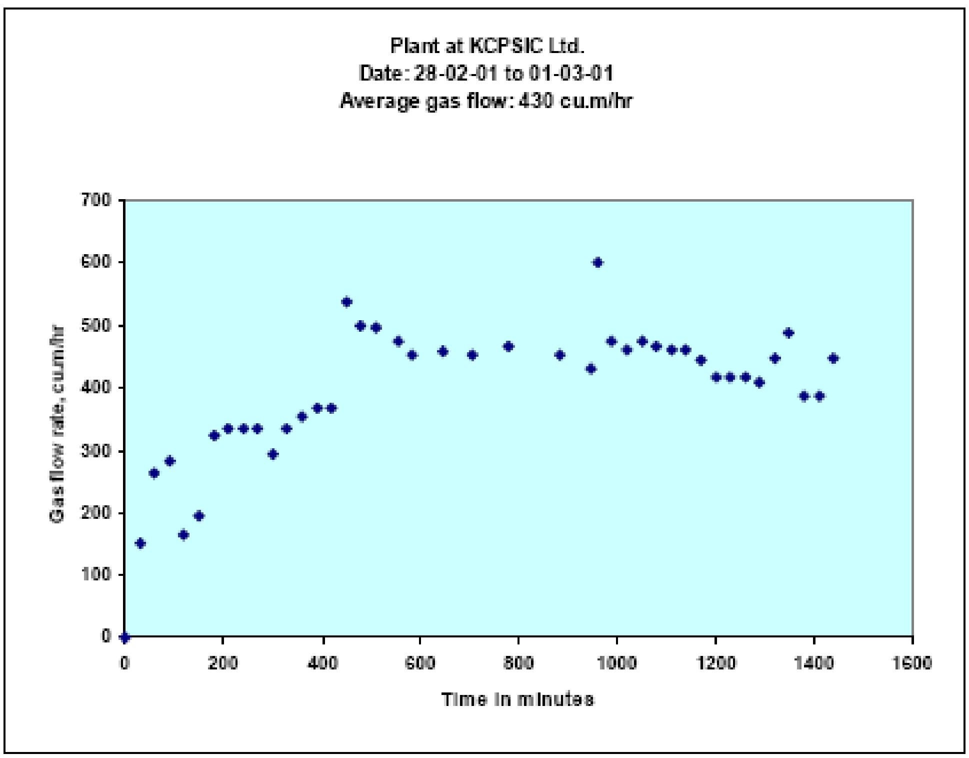


Fig 5. Typical plant loading of Hydrogen sulphide scrubbing system

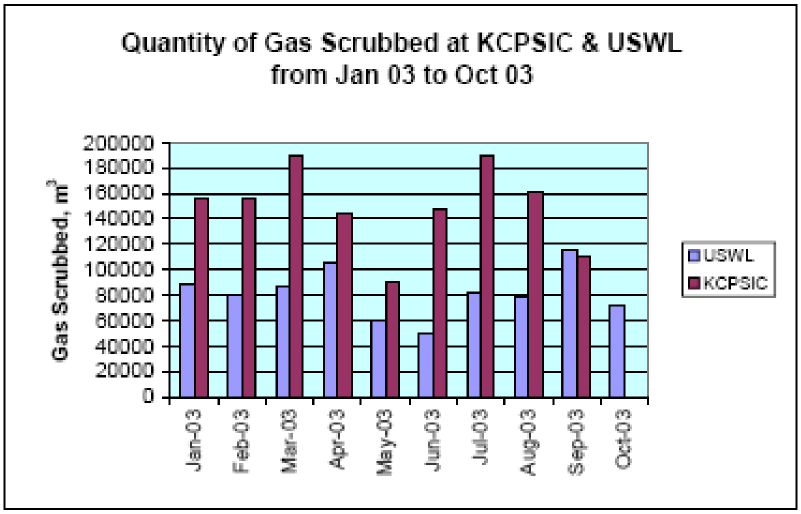


Fig 6. Gas Scrubbed

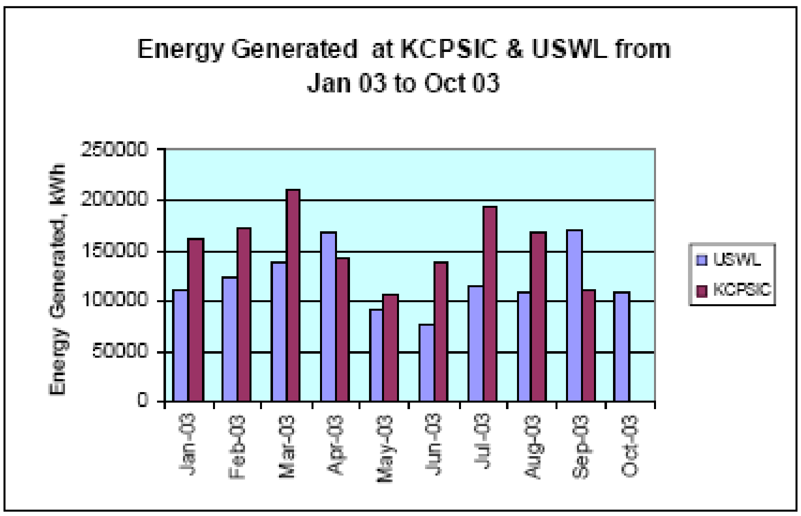


Fig 7. Power Generated

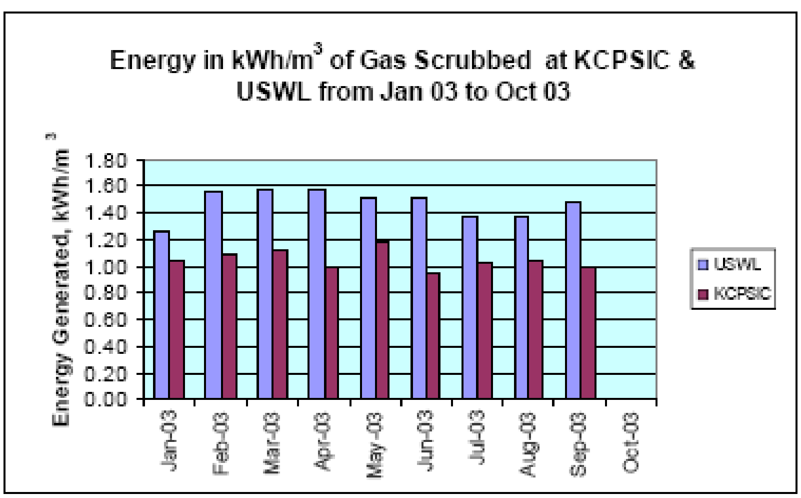


Fig 8. Energy per m^3 of gas scrubbed

Techno-economics for Biogas power plant with ISET process for Hydrogen sulfide scrubbing (H_2S concentration - 3.0 %)

Serial No.	Description	Cost in Million Rs		
		0.5 MWe	1.0 MWe	2.0 MWe
1	Gas Engine directly coupled with alternator, 50 Hz with controls	8.0	15.0	28.0
2	*ISET* H_2S scrubber	6.0	10.0	18.0
3	Building and Infrastructure	2.0	3.5	5.0
4	**Capital Investment (1+2+3)**	**16.0**	**28.5**	**51.0**
5	Energy generated at 7000 hrs running time per year (million units)	3.5	7.0	14.0
6	In-house energy consumption for 7000 hrs running time per year(million units)	0.3	0.6	1.2
7	**Revenue earned per annum by power generation at energy cost of Rs. 4.0/kWh**	**14.0**	**28.0**	**56.0**
8	Scrubber running expenditure including salary	3.0	5.5	10.5
9	Engine operating cost including salary	1.0	2.0	3.5
10	**Revenue generated by sulfur sale @ Rs 0.06/kWh**	**0.21**	**0.42**	**0.84**
11	Interest rate of 12.0 % for Loan repayment in 10 years	1.8	3.3	5.9
12	Linear Depreciation for 10 years considering 10 % salvage value	1.35	2.5	4.4
13	**Revenue earned per annum after accounting running cost, loan repayment and depreciation**	**7.05**	**15.10**	**32.5**
14	**Pay Back period in years**	**2.3**	**1.9**	**1.6**

Pay back period is 1/3rd compared to other red-ox processes outside the country.

* *Techno-Economics is based on Indian Conditions.*

* *The biogas has not been priced as it is a by-product from a mandatory ETP setup by the Industry.*