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Prospects for petcoke utilization with CO_2 capture in Mexico

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Abstract

This paper evaluates the introduction of carbon capture and storage (CCS) to Mexico. The gasification technology is presented as a potential alternative to be applied into refinery plants due to high petcoke production. Although economic aspects, such as fuel price and selling CO_2, are important in the selection of CCS alternatives, there are other limitations, i.e. water availability and space. In March 2014, Mexico launched its CCS technological roadmap. However, an evaluation of the installation of new CO_2-capture ready power plants was not considered. For that reason, this study could be useful to create a technology roadmap that includes the design of CO_2 capture plants into refineries and how they will have to operate for CO_2 emissions reduction, and taking advantage that most of refineries and petrochemical plants are close to oil fields for enhanced oil recovery (EOR). Integrated gasification combined cycle (IGCC) with CCS was chosen in this paper for power generation using petcoke as feedstock. The emissions of CO_2 in kg/kWh could be reduced by 68%.

Keywords: CCS-EOR; Mexico; petcoke; gasification technology; refineries and petrochemical plants

1. Introduction

In Mexico, greenhouse gas (GHG) emissions of 748.3 $MtCO_{2\text{-eq}}$ were reported in 2010, where 67.3% of those are attributed to the energy sector– of this sector, the petroleum and gas sectors accounted for 16.6% and the transport sector for 22% [1].

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Nomenclature

ASU	air separation unit	IGCC	integrated gasification combined cycle
CCS	carbon capture and storage	PEMEX	Mexican Petroleum
CCUS	carbon capture, utilization and storage	NGCC	natural gas combined cycle
CFB	circulating fluidized bed	WGS	water-gas shift
EOR	enhanced oil recovery		

Petróleos Mexicanos (PEMEX), one of the two major Mexican energy companies, emitted 45 $MtCO_{2eq}$, representing 6% of the total GHG emissions [1]. Mexico is opportunely committed to reducing its CO_2 emissions; whilst the exploitation of oil sites soon to decrease in productivity using traditional extraction techniques could be extended by CO_2 injection for enhanced oil recovery (CO_2-EOR). CO_2-EOR into depleted oil fields improves the flow and recovery rate of hydrocarbons. As a result, CO_2-EOR may provide two benefits: increase Mexico's oil production and reduce GHG emissions [2]. In March 2014, Mexico launched its CCS technological roadmap, which contains the actions to be taken until 2024 [3]. However, CO_2 capture and EOR readiness for new power plants were not considered. Lacy et al. [2] evaluated the potential of CCS on existing power plants in Mexico, but they did not consider forthcoming projects either. In the oil industry, the refinery residual, petcoke from delayed coking units, is considered in this paper for gasification and power generation with reduced CO_2 emissions by integrating CCS.

1.1. CO_2-EOR in Mexico

CO_2 sources nearby the oil reservoir sites have been identified to evaluate the potential for CO_2-EOR. Petrochemical, refinery and gas processing plants were responsible for 40.63 $MtCO_2$/y emissions in 2013 [1]. Potential industrial sources with CO_2 emissions above 0.5 $MtCO_2$/y are located within 180 km of oil fields Chicontepec and Cinco Presidentes in the Gulf of Mexico [2]. These could supply a large fraction of the demand of CO_2 for EOR, estimated to be 50 $MtCO_2$/y [3]. Table 1 shows the major CO_2 sources with their CO_2 purity nearby the oil field Cinco Presidentes as candidate for EOR and identified by PEMEX. Since the ammonia plant already produces a high purity CO_2 stream, successful EOR pilot tests have been performed at the oil field Coyotes.

Table 1. CO_2 availability and quality (at 1 atm and 0°C) in Cinco Presidentes [1].

Source	Location	CO_2 emissions (Mm^3/day)	CO_2 purity (% vol.)
Ammonia	Cosoleacaque	1.22	97
Ethylene oxide	Morelos and Cangrejera	0.09	97
Hydrogen	Minatitlan	0.36	77 (% wt.)
Ethylene	Morelos, Cangrejera, and Pajaritos	1.48	13 (% wt.)
Sulfur Plants	Cactus, Nuevo Pemex, and Cd. Pemex	1.87	22
Petrochemical complex	Morelos, Cangrejera, Pajaritos, and Cosoleacaque	5.24	8 – 11
Gas processing complex	Cactus, Nuevo Pemex, Cd. Pemex, and La Venta	3.83	8 – 11
Refinery in Minatitlan	Minatitlan	1.16	8 – 11
Total		15.24	

1.2. Petcoke

Petcoke is a refinery residual product from delayed coking units. As part of the refining of oil, crude oil is converted into gasoline, diesel fuel, jet fuel, lubricating oils and waxes; and as a by-product, residual crude is produced. The crude residue may be further refined in the so-called coking process, where large hydrocarbon molecules are broken down to yield petcoke. In Mexico, petcoke is currently consumed by the industrial sector, mainly by the cement industry, and in lower proportion by the metal, chemical, and metallic and electrical product industries, due to its relatively cheap cost. Petcoke price is expected to decrease from 1.8 US$/mmBTU in 2012 to 1.18 US$/mmBTU by 2027 [4].

The private electricity sector has increased petcoke consumption by partly replacing fuel oil usage. The use of petcoke for electricity generation increased from 2342 to 4220 GWh during 2004 to 2014 [5]. The private electricity sector consumed 17,400 barrels (equivalent to crude oil) of petcoke and the industrial sector 45,300 barrels in 2012. Petcoke production was 2.58 Mt, from the refineries in Cadereyta (37.5%), Minatitlan (32.8%), and Madero (29.7%) in 2012. However, the demand of petcoke is not fulfilled only by production, thus petcoke is imported. Thus, petcoke production is expected to nearly fulfil the demand by 2021. The projects planned to increase its production include the reconfiguration of the refinery in Minatitlan, coking projects in the refineries of Cadereyta and Madero, and the new operation capacity of the distillation and conversion of residuals in the refinery of Salamanca.

Interest on integrated gasification combined cycle (IGCC) has expanded in the last years to refinery residuals, such as vacuum residues, heavy fuel oil, asphalt and petcoke. This interest has started because minor components of the produced syngas are easier to remove than those pollutants from direct combustion, and the syngas can be utilised to produce chemicals, steam and/or power. Three technologies have been proposed for power and stream generation using petcoke as fuel: conventional boilers with flue gas desulfurization, circulating fluidized bed (CFB) boilers, and IGCC [6]. These technologies were recommended with the aim of proposing new cogeneration plants using residual fuels from refineries nearby; however, the CO_2 capture was not evaluated. Therefore, IGCC with CCS was the technology chosen in this paper for power generation using petcoke as feedstock.

1.3. Space to incorporate CCS projects

In refineries, CCS would be applied to existing plants. Refineries and petrochemical complexes have more issues than natural gas power plants in relation to surrounding available space, since they are in close proximity to towns. For instance, the petrochemical complex in Cosoleacaque, Ver. has no free space because of its location inside an urban zone (see Figure 1).

Fig. 1. PEMEX Petrochemical complex Cosoleacaque

1.4. Gasification

Gasification is a technology that has experienced a significant growth in capacity since the early 2000s. It was reported by the Gasification Technologies Council (GTC) that 385 gasifiers were in operation in 2004 with a syngas output of 43 GW_{th}, and those numbers have increased to 618 gasifiers in active operation with an output of 104.7 GW_{th} by October 2013; plus 202 gasifiers were counted as under construction to supply additionally 63.4 GW_{th} [7]. The main products of gasification are chemicals, followed by liquid and gaseous fuels, whilst the power industry is not showing a significant increase due to lack of CO_2 legislation and emergence of shale gas [8].

Gasifiers are classified based on the bed type, as: fixed-bed gasifiers, fluidised bed gasifiers, and entrained flow gasifiers. These types of gasifiers have been described in detail elsewhere [9, 10]. Based on the installed gasifiers and feedstocks employed, it is expected that entrained gasifiers, which can handle any type of coal, will be preferred for petcoke applications using IGCC in Mexico. Table 2 shows commercial entrained flow gasifiers that are operating, or planned to start operation, using petcoke as feedstock. GE Energy technology uses a single-stage refractory-lined reactor to produce syngas. Slurried feedstock (coal/water slurry ~65% wt.) and oxygen enter to the gasifier from the top; and heat is recovered by cooling the syngas produced by water quench or radiant cooler [11].

Table 2. Commercial Entrained Flow Gasifiers using petcoke as feedstock [7].

Technology Name	Plant Name	Country	Main Product	Gas cleanup / Sulfur removal	Start year
CB&I E-Gas	Wabash River IGCC	United States	Power (262 MWe)	MDEA / Claus	1995
GE Energy	Coffeyville Syngas Plant	United States	Chemicals (Ammonia)	Selexol/ Claus/ Ammonium thiosulphate	2000
GE Energy	Ube City CO Plant	Japan	Chemicals (CO)[1]	NA	1982
MHI Gasifier	Hydrogen Energy California	United States	Power (300 MWe)	NA	2016
GE Energy	Lake Charles Clean Energy project	United States	Chemicals (Methanol, H_2)	Rectisol / WSA	2016
CB&I E-Gas	Jamnager Gasification plant phase II	India	Gaseous fuels (SNG, H_2)	NA	2017
NA	Panama Urea Fertilizer Plant	Panama	Chemicals (Ammonia, urea)	NA	2017

[1] CO is used to produce oxalic acid
NA: not available
MDEA: Methyl diethanolamine
WSA: wet sulfuric acid process

The E-Gas™ technology is now owned by CB&I, consisting of a pressurized gasifier designed for upflow, entrained-flow slagging and two-stage operation. This gasifier also uses a slurry-feed system of concentrations in the range of 50 to 70%, which depends on the moisture and quality of the feedstock. Part of the slurry feed and oxygen are introduced to the first (or bottom) stage of the gasifier. Therefore, in this stage oxidation reactions occur and due to its exothermic nature operating conditions are at about 1,400°C and 25 bar. The hot syngas leaving the first stage is then introduced into the second top stage where the remaining slurry feed is introduced. The second oxygen-free stage can be configured for a desired H_2/CO ratio and methane content [11].

The MHI gasifier also consists of a pressurized, upflow, entrained-flow slagging reactor with two-stage operation as the E-Gas™ gasifier, however, it uses a dry-feed system instead, and the reactor internal is protected by a membrane wall [12]. For IGCC using petcoke as fuel, entrained gasifiers are recommended. As a result, this work presents some calculations for IGCC with carbon capture to evaluate the reduction of CO_2 emissions.

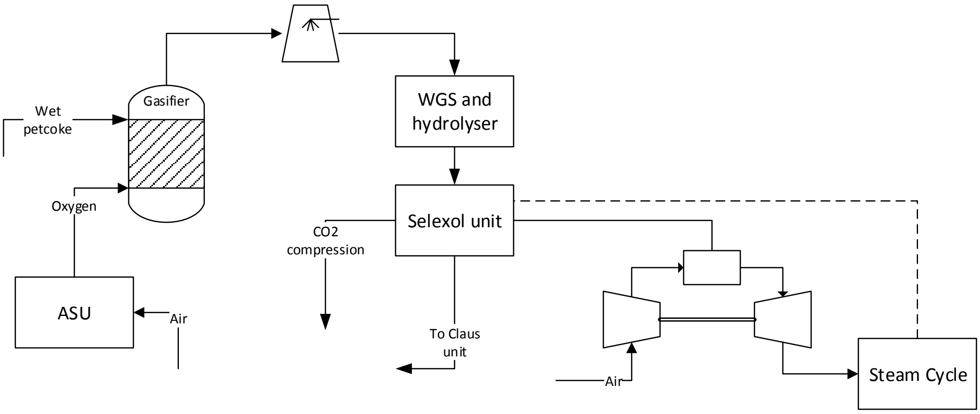
2. IGCC evaluation

Some commercial-scale pre-combustion carbon capture plants have been installed worldwide. For example, the Kemper County pre-combustion IGCC plant in USA that uses lignite to generate up to 524 MW. Physical absorption, e.g. Selexol and Rectisol processes, is the preferred CO_2 capture technology due to its maturity and lower costs [13]. Figure 2 shows the main components of the IGCC plant. Following the methodology in [14], the gasifier was simulated using an RGibbs reactor modelled in Aspen Plus® that minimizes the Gibbs free energy. The gasifier was set with a restricted-equilibrium approach, where the reaction temperature approaches were specified to agree with industrial data for the GEE-type entrained-flow gasifier with Illinois No. 6 coal as fuel [15]. It was assumed that there was a 98% carbon conversion and the reactions previously proposed occur. In this evaluation, petcoke was used in the simulations, with the properties shown in Table 3.

Based on the estimated production of petcoke for 2013–2027 from a refinery in Minatitlan, Cadereyta or Madero [2], a petcoke flow rate of 85.6 tons/h was chosen for an IGCC with CO_2 capture plant. The gasifier is operated at 1315.6°C and 5.61 MPa, with a H_2O/petcoke ratio of 0.422 and O_2/petcoke of 0.832. Oxygen produced in an air separation unit (ASU) with 95% (mol) purity is used as gasifying agent. The syngas is directed to a water-gas shift (WGS) reactor and hydrolyser to convert 87.5% of CO to CO_2. Then, the flue gas is cleaned in a Selexol unit where 98.3% of CO_2 is captured.

Table 3. Properties of the petcoke used in the model. [1] From [6]

Proximate Analysis (weight %, as received)		Ultimate Analysis (weight %, dry)[1]	
Moisture[1]	10.60	Ash	0.30
Ash	0.27	Carbon	89.20
Volatile Matter	10.00	Hydrogen	3.70
Fixed Carbon	79.13	Nitrogen	1.80
HHV (MJ/kg)[1]	31.3	Sulfur	5.00



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3. Results and Discussion

The main purpose of the modelling of Figure 2 is to assess the potential utilization of petcoke in an IGCC process with CO_2 capture. Based on the specifications described in section 2, Table 4 shows that the flue gas composition and how hydrogen concentration increased after each stage: gasification, WGS reaction and hydrolysis, and CO_2 removal. The cleaned syngas consists mostly of H_2, which could be mixed with natural gas in order to increase the HHV, and then directs the gas turbine to generate power.

Table 4. Flue gas composition of gas streams at different stages of the IGCC plant (% mol).

Component	Syngas	WGS reactor and hydrolyser	Cleaned syngas
CO	45.8	4.3	7.2
CO_2	11.9	38.8	1.1
N_2	0.7	0.5	0.8
H_2	30.8	52.8	89.4
CH_4	0.1	0.1	0.2
H_2O	8.3	1.7	9.8×10^{-3}
H_2S	1.2	0.9	3.8×10^{-4}
HHV (MJ Nm^{-3})	9.73	7.21	11.75

Table 5 compares IGCC power plants without and with CCS, and shows the benefits of adding CCS in order to reduce CO_2 emissions. For comparison purposes, the plant was first run using the same petcoke flow as in [6]. IGCC delivers higher power and lower CO_2 emissions than CFB technology [6]. Moreover, the integration of carbon capture drops CO_2 emissions by 68%, but at the expense of a decrease in the net power output by 20%. The capture plant removes 172 tonnes/h of CO_2, and the CO_2 emissions into the atmosphere derive from two sources: the flue gas exiting the steam cycle and emitting 25.6 tonnes/h of CO_2 at 139°C, which is above the cold end corrosion temperature; and the CO_2 emissions from the Claus unit at a similar rate of 25.5 tonnes/h.

The results presented will benefit of an integration of CO_2 is capture at the source with CO_2 used for enhanced oil recovery in nearby oil fields and finally geologically stored. This proposed solution could complement a previous CCUS study focused on NGCC facilities due to the low cost of natural gas in order to tackle CO_2 emissions. That work showed a 64% reduction in CO_2 emissions when post-combustion is integrated to the NGCC plant [16].

Table 5. Comparison of CFB, IGCC and IGCC with CO_2 capture.

	Petcoke (t/h)	Power (MW)	CO_2 emissions (kg/kWh)	Reference
IGCC	68.6	237.2	0.673	[6]
IGCC with carbon capture	68.6	189.3	0.215	This work
IGCC with carbon capture	85.6	237.8	0.215	This work

4. Conclusions

The key findings can be summarised as follows:

- IGCC represents a viable option to utilise refinery residuals such as petcoke to generate electricity for the plant and neighbours;
- IGCC, integrated with the CCS technology, could reduce CO_2 emissions and the CO_2 captured could be used for EOR. In the gasifier, it is possible to remove the CO_2 from the syngas. CO_2 emissions are reduced by 68% (in kg/kWh) due to emissions from Claus unit and gas turbine;
- Entrained flow gasifiers are preferred for fuels such as petcoke, and the ash by-product (inert slag) can be sold as a construction material;
- Entrained flow gasifiers operate with oxygen (95%) as a gasifying agent. This is an advantage for integration with CO_2 capture since the syngas produced contains a very small concentration of nitrogen (see Table 4);
- The evaluation of how much CO_2 is reduced using this technology should be evaluated taking into account the CO_2 emitted by the gas turbine. This will be defined in future work.

Future research will involve a techno-economic assessment of the system and the effects of varying the assumed percentage conversion of CO into CO_2 in the WGS and hydrolyser stage.

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