

# **A Graphical CO<sub>2</sub> Emission Treatment Intensity Assessment for Energy and Economic Analyses of Integrated Decarbonised Production Systems**

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## **Abstract**

Design of clean energy systems is highly complex due to the existence of a variety of CO<sub>2</sub> abatement and integration options. In this study, an effective decision-making methodology has been developed for facilitating the selection of lowest energy **or** lowest cost intensity systems, from a portfolio of flowsheet configurations with different decarbonisation strategies. The fundamental aspect of the proposed methodology lies in thermodynamic feasibility assessment as well as quantification of CO<sub>2</sub> emission treatment intensity using a graphical approach (CO<sub>2</sub> emission balance diagram) for energy and economic performance analyses of integrated decarbonised systems. The relationship between the graphical representation and performances is established using Blocks and Boundaries on integrated systems. The effectiveness of the methodology has been demonstrated through a range of coal gasification based polygeneration and cogeneration systems, incorporating either of carbon capture and storage (CCS) or CO<sub>2</sub> reuse options.

*Keywords:* clean coal technology; coal to liquid fuel synthesis; CO<sub>2</sub> reuse; polygeneration; carbon capture and storage; process integration

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## 1. Introduction

CO<sub>2</sub> abatement system in the context of clean energy production has received considerable attention in recent times. Stringent environmental regulation has been enforced as an essential measure in mitigating greenhouse gases and tackling global warming. The implementation of carbon tax in industrialised countries directly affects the economic performances of fossil fuel plants. In the context of chemical conversion of CO<sub>2</sub>, CO<sub>2</sub> abatement system consists of a capture process with links to storage or reuse system. Carbon capture and storage (CCS) technologies in pre-combustion, post-combustion and oxy-combustion routes are the leading CO<sub>2</sub> abatement systems. The captured CO<sub>2</sub> is subsequently transported and stored underground (IPCC, 2005). CCS has been commercialised but has not yet been widely employed attributed to various uncertainties in geologic carbon storage and consequently high infrastructural cost. Chemical looping is an emerging CO<sub>2</sub> capture technology (Fan et al., 2008). The concept involves conversion of gaseous carbonaceous fuels via redox (reduction-oxidation) reactions, by using metal oxide composite particles. The technology has been broadly practised in combustion processes for power generation and thus known as chemical looping combustion (Jerndal et al., 2006). In light of the advantages of capturing CO<sub>2</sub> effectively and avoiding the use of expensive air separation unit, the chemical looping concept enables clean coal gasification processes without any significant reduction in energy efficiency. Thus it can be further extended into syngas chemical looping process, producing hydrogen, electricity as well as transportation fuels (Gupta et al., 2007; Tomlinson et al., 2007). Another alternative route for mitigating CO<sub>2</sub> is via reusing CO<sub>2</sub> into the production of other useful chemicals or fuels. This route is still under explored due to uncertainties in thermodynamic and economic feasibility with respect to the conversion of highly stable CO<sub>2</sub>.

The two most prevalent process integration techniques, i.e. heat integration (Linnhoff et al., 1994; Smith, 2005) and mass integration (El-Halwagi, 1997) have widely been adopted in the fields of energy savings and pollution reduction. The combined heat and mass integration analyses into targeting power cogeneration potential as well as utilisation of combustible waste have been studied by El-Halwagi et al. (2009). El-Halwagi et al. (2003) devised a material reuse strategy using effective graphical targeting approaches to minimise the consumption of fresh resources. Linnhoff and Dhole (1993) proposed a CO<sub>2</sub> emission targeting approach for total site, with the consideration of trade-offs between process fuel and steam, between steam, site fuel and cogeneration and fuel mix. Tan and Foo (2007) developed a new application of graphical pinch analysis for carbon-constrained energy sector planning, known as “carbon emission pinch analysis (CEPA)”, extending the scopes to a wider context, i.e. from an industrial site to a regional or national energy sector. Zhelev and Ridolfi (2006) presented a holistic decision-making tool for resource management by utilising combined energy (considering environmental and economic values) and pinch concepts (considering thermodynamic aspect). Klemeš et al. (2007) presented a whole system techno-economic modelling approach to assess the cost of carbon capture in coal-fired power station. Friedler et al. (1993) introduced a P-graph methodology for systematic synthesis of process networks with an aim of obtaining optimum structures based on economic benefits. Friedler (2010) provided a comprehensive review of the early stage and state-of-the art process integration techniques for solving energy and pollution related problems. In their works, process economics are a key consideration in the implementation of CO<sub>2</sub> abatement strategies into an energy system. A variety of CO<sub>2</sub> abatement options are possible, leading to various complex flowsheet configurations. In addition, their application on a full scale is uncertain due to potential thermodynamic and economic implications. It is widely recognised that an effective however shortcut methodology is imperative for analysing the feasibility of

integration of CO<sub>2</sub> abatement options, embracing CO<sub>2</sub> reuse or CCS into coal gasification system. The proposed effective and shortcut methodology for the selection, decision-making and integration of CO<sub>2</sub> abatement processes into an energy system can be used for grassroots as well as retrofit designs. Screening is an important aspect in the context of the above primary objectives of the methodology. This requires comparison of distinctive thermodynamic and economic features between various flowsheet configurations. Consequently, the energy and economic performances of integrated CO<sub>2</sub> abatement and energy systems are built upon the interpretation of CO<sub>2</sub> treatment intensity standpoint.

Five coal gasification process schemes with various CO<sub>2</sub> abatement strategies are exemplified to demonstrate a fundamental relationship between an integrated system performance and its emission treatment intensity index (ETII). The systems under consideration as follows: polygeneration with CCS system (Case A); polygeneration with CO<sub>2</sub> reuse into methanation process (Case B); integrated gasification combined cycle (IGCC) with CCS (Case C); modified IGCC with CO<sub>2</sub> reuse into syngas generation via tri-reforming process and further into methanol synthesis (Case D); syngas chemical looping (Case E), are illustrated in Appendix A. Polygeneration represents an integrated system which utilise one or more feedstocks to generate multiple products (Liu et al., 2007; Liu et. al, 2009; Liu et al. 2010). The polygeneration concept provides several advantages such as flexibility in production suitable for the contemporary market needs as well as self-satisfied environment by on-site generation of heating and cooling. It is regarded as a promising solution in meeting the future energy demand while mitigating the environmental pollution.

The paper contributes to the following tools:

- A shortcut methodology comprising of thermodynamic and economic feasibility assessment.
- A systematic graphical representation that features the generation and removal of CO<sub>2</sub> of all the concerning process units within a system, coined as “Emission balance diagram (EBD)” for the quantification of the treatment intensity of CO<sub>2</sub> abatement system, ETII.
- Block and Boundary concept, combined with shortcut energy auditing and economic evaluation approaches for deriving the relationship between ETII and plant performances.

## **2. Methodology**

CCS and CO<sub>2</sub> reuse are the two main CO<sub>2</sub> abatement strategies. The selection of an appropriate CO<sub>2</sub> abatement strategy for an energy system remains a great challenge since numerous CO<sub>2</sub> conversion pathways and their integration synergies with the parent system exist. Within the consideration of CO<sub>2</sub> reuse route, there are numerous CO<sub>2</sub> conversion pathways leading to an exhaustive number of design configurations. This section presents an overview of the methodology using thermodynamic screening based on Gibbs energy assessment and EBD and ETII for ranking of integrated options according to cost and energy intensities.

### *2.1 Overview of Methodology*

Figure 1 presents a shortcut approach for investigating the impact of integration of CO<sub>2</sub> abatement facility (CCS or CO<sub>2</sub> reuse) to a system. This methodology allows flexibility in product generation and CO<sub>2</sub> conversion pathways, not necessarily driven by market values

of products, but also by thermodynamic and CO<sub>2</sub> treatment intensities. It uses distinctive thermodynamic and economic performance features with an acceptable level of accuracy for screening and decision-making amongst various integrated systems. The selected flowsheet can further be analysed using simulation modelling, mass and heat integration and detailed economic assessment.

**Figure 1**

To enhance the selection procedure and effective decision-making of which design is more appropriate, the proposed methodology comprises of the following two steps:

- (1) The Gibbs energy method is used to screen out the thermodynamically non-favourable pathways for CO<sub>2</sub> conversion. (section 2.2)
- (2) EBD is constructed featuring the mass fraction and mass load of CO<sub>2</sub> generated / consumed. A mass and energy balance or a basic simulation model for the mass and energy balance of integrated flowsheets is developed. ETII is predicted to estimate the plant performances of integrated decarbonised systems. (section 2.3)

The relationship between ETII and the energy and cost intensities of integrated CO<sub>2</sub> abatement systems is established using Block and Boundary concept, detailed in section 3. This leads to the investigation of a range of coal gasification systems with different CO<sub>2</sub> abatement strategies in section 3. The proposed shortcut methodology is capable of screening thermodynamically and economically favourable CO<sub>2</sub> abatement routes in order for feeding these configurations into detailed process integration and optimisation studies.

## 2.2 Thermodynamic Screening Assessment using Gibbs Energy Method

CO<sub>2</sub> is a highly stable component and most of the reactions converting CO<sub>2</sub> are energetically unfavourable (Xu and Moulijn, 1996). Therefore, Gibbs energy method is adopted for evaluating thermodynamic spontaneity of CO<sub>2</sub> conversion pathways (Kondepudi, 2008). In this study, four illustrative reactions in equations (1)-(4) in Table 1 have been selected for thermodynamic screening. The thermodynamic data required for estimating the enthalpy change and Gibbs energy change of reactions are given in Appendix B. These reactions encompass the production of methane (equation (1)), methanol (equation (2)), formic acid (equation (3)) and syngas (equation (4), dry reforming process) utilising CO<sub>2</sub>.

### **Table 1**

According to the results summarised in Table 1, the reactions in equations (1)-(3) are exothermic and the reaction in equation (4) is endothermic. For a reaction to proceed spontaneously, the Gibbs free energy should decrease ( $\Delta G_R^\circ < 0$ ) at constant temperature and pressure, alongside an increase in entropy change  $\Delta S$ . The methane production in equation (1) is energetically favourable due to strong negative  $\Delta G_R^\circ$ . The methanol production in equation (2) is thermodynamically less favourable since the reaction has a lower negative  $\Delta G_R^\circ$ . The formic acid formation reactions in equation (3) and dry reforming reaction in equation (4) are not thermodynamically spontaneous due to positive  $\Delta G_R^\circ$ .

Sensitivity analyses are carried out to assess the temperature dependency of the Gibbs free energy. The feasibility of a reaction within a range of operating temperatures is thus predicted. Since the reuse of CO<sub>2</sub> often involves liquid product formations, variation in Gibbs energy with respect to pressure may not be significant. The temperature dependency of the Gibbs free energy change with the enthalpy change is demonstrated by Gibbs-Helmholtz

equation (5) (Kondepudi, 2008). Equation (6) shows the integrated form derived from the differential form of equation (5) for estimating the  $\Delta G_R$  at a specific temperature, assuming that  $\Delta H_R$  has negligible variation with temperature. The variation in  $\Delta G_R$  with respect to  $T$  is illustrated in Figure 2. Figure 2 provides information regarding the range of operating temperature where a reaction may occur (constant pressure is assumed at 1 atm). The reactions in equations (2) and (3) are not likely to proceed at any temperature since  $\Delta G_R$  is always in the positive region. A temperature lower than 610 K favours the reaction in equation (1), while a temperature greater than 960 K helps the reaction in equation (4) to proceed spontaneously. Equation (7) can be used for predicting  $\Delta G_R$  at a particular pressure, where ideal gas law is applied.

$$\left(\frac{\partial(\Delta G_R/T)}{\partial T}\right)_p = -\frac{\Delta H_R}{T^2} \quad (5)$$

$$\left(\frac{\Delta G_R}{T}\right)_{T_2} = \left(\frac{\Delta G_R}{T}\right)_{T_1} + \Delta H_R \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (6)$$

$$\Delta G_R(p_2) = \Delta G_R(p_1) + nRT \ln\left(\frac{p_2}{p_1}\right) \quad (7)$$

where  $T_1$  and  $T_2$  are the initial and final temperatures;  $p_1$  and  $p_2$  are the initial and final pressures, respectively.  $n$  is the number of mole.  $R$  is the universal gas constant (0.008314 kJ/mol-K).

### **Figure 2**

In conclusion, the conversion of CO<sub>2</sub> into the formation of methanol (equation (2)) and formic acid (equation (3)) formation are not thermodynamically favourable under the investigated temperature conditions. The formation of methane (equation (1)) is



thermodynamically spontaneous at a lower temperature range of 298 - 610 K, while syngas production from CO<sub>2</sub> (equation (4)) is energetically favourable provided that it is carried out at a high temperature range of 960 - 1200 K.

### *2.3 Emission Balance Diagram and Emission Treatment Intensity Index*

A systematic graphical representation, EBD, is proposed for analysing the CO<sub>2</sub> generation and removal from every process unit within a system. EBD of CO<sub>2</sub> comprises of two profiles, CO<sub>2</sub> generation and CO<sub>2</sub> removal profiles. The mass fraction of CO<sub>2</sub> is plotted against the mass load of CO<sub>2</sub>, resulting in a step-down chart. A general EBD is illustrated in Figure 3.

#### **Figure 3**

The concept behind construction and usefulness of EBD is as follows.

1. The generation and removal profiles are presented by horizontal steps in the order of decreasing mass fraction of emission component and cumulative mass loads. The mass fraction of the emission component at the outlet gaseous streams from the generation (from reaction) or removal (stored / emitted / reused) processes is plotted against its corresponding mass load. Both profiles should end at the same point in abscissa as their total mass loads are the same thus achieving CO<sub>2</sub> mass balance within a process plant. The method is built upon the 'path diagram' introduced by El-Halwagi (1997) where the flow of a species in each stream is tracked through a path. The EBD however concerns with the points where there are changes in the amount and concentration of emission component due to generation or removal.

2. This diagram can be used in targeting for emission minimisation such as through manipulation of related process operating conditions. Furthermore, it can be used for analysing the CO<sub>2</sub> treatment intensity within a process plant, discussed as follows.

ETII is introduced as a quantitative parameter for classifying emission treatment processes, i.e. CO<sub>2</sub> treatment in this context, based on the area confined between the generation and removal profiles. The derivation of ETII is demonstrated as follows:

Let the functions of the generation and removal profiles be  $\lambda_j(l_j)$  and  $\mu_k(m_k)$ , respectively.  $l_j$  and  $m_k$  represent the mass loads of CO<sub>2</sub> within a step,  $j$  or  $k$  in the generation and removal profiles, respectively.  $U$  and  $W$  are the total number of steps in the generation and removal profiles, respectively.

Area between the generation and removal profiles

= Area under generation profile  $A(\lambda)$  – Area under removal profile  $A(\mu)$

$$\begin{aligned}
&= \sum_{j=1}^U \int_{l_{j-1}}^{l_j} \lambda_j(l_j) dl_j - \sum_{k=1}^W \int_{m_{k-1}}^{m_k} \mu_k(m_k) dm_k \\
&= [\alpha_1(l_1 - 0) + \alpha_2(l_2 - l_1) + \dots + \alpha_U(M - l_{U-1})] - [(\omega_1(m_1 - 0) + \omega_2(m_2 - m_1) + \dots + \omega_W(M - m_{W-1}))]
\end{aligned} \tag{8}$$

$\alpha$  and  $\omega$  are the mass fractions of CO<sub>2</sub> in the generation and removal profiles, respectively.  $M$  is the total mass load of CO<sub>2</sub> shown as the final point on the profile.

Assuming that the generation profile lies above the removal profile, the area between the two profiles, defined in equation (8) should have a value greater than zero. Transforming equation (8) into a dimensionless form, equation (9) can be obtained.

$$\frac{\sum_{j=1}^U \int_{l_{j-1}}^{l_j} \lambda_j(l_j) dl_j - \sum_{k=1}^W \int_{m_{k-1}}^{m_k} \mu_k(m_k) dm_k}{\sum_{k=1}^W \int_{m_{k-1}}^{m_k} \mu_k(m_k) dm_k} = \frac{A(\lambda) - A(\mu)}{A(\mu)} = \frac{A(\lambda)}{A(\mu)} - 1 > 0 \tag{9}$$

ETII is defined as the ratio between the area under the generation profile,  $A(\lambda)$  and the area under the removal profile,  $A(\mu)$ , shown in equation (10).

$$ETII = \frac{A(\lambda)}{A(\mu)} \quad (10)$$

Therefore, if the generation profile is placed above the removal profile (CO<sub>2</sub> reuse case), ETII should have a value greater than 1. If there is a case where the generation profile lies below the removal profile (storage case), then ETII should be less than 1. Higher ETII for CO<sub>2</sub> reuse cases is desirable and vice versa for storage cases. Both directions imply to lower total plant investment (TPI) and higher overall net energy, explained later in section 3.4.

### **3. Derivation of the Relationship between Emission Treatment Intensity Index and Plant Performances**

#### *3.1 Block and Boundary Concept*

A block and boundary concept is introduced for the design prioritisation and scoping analysis between similar plant types (e.g. coal gasification) with different production routes and process configurations. In this approach a process flowsheet is divided into key blocks, each comprising of a group of processes dedicated to perform a task or to achieve an objective, e.g. syngas generation, gas cleaning, CO<sub>2</sub> reduction, etc. The philosophy is to compare thermodynamic and economic performances between similar functioning blocks, though containing different process configurations, in different flowsheets. Thus, a number of similar functioning blocks and boundaries in various flowsheets are identified. Typically, a coal decarbonised polygeneration plant has 4 key blocks, syngas generation and cleanup, CO<sub>2</sub> separation, CO<sub>2</sub> disposal (storage / reuse) and production (cogeneration / polygeneration), respectively illustrated in Figure 4. It is recommended that the number of blocks within a

system should be kept to a minimum number to avoid losing practicability of the screening approach.

#### **Figure 4**

### *3.2 Case Studies*

The ASPEN Plus simulation flowsheets of five coal gasification Cases A-E with different CO<sub>2</sub> abatement integration synergies are illustrated in Figure 5(a)-(e). The process descriptions are provided in Appendix A.

#### **Figure 5**

Figure 5(a) presents a coal polygeneration system with CCS, Case A, producing electricity, hydrogen, acetic acid and methanol. Figure 5(b) is a modification of Case A, wherein captured CO<sub>2</sub> is reused into methanation process (Case B). The blocks and boundaries I to IV across processes that exhibit similar functionality are classified for each flowsheet. Block I encompasses the GASIFIER, CYCLONE, water-gas shift (WGS) reactor, water (H2OREM) and H<sub>2</sub>S removal (H2SREM) processes. CO<sub>2</sub> capture system (CO2SEP) is contained in block II. Block III represents the CO<sub>2</sub> storage / reuse process. Block IV encapsulates all production routes mainly consisting of reaction and separation processes. After grouping similar functional processes into individual blocks in a flowsheet, it is clear that only block III is different between Cases A and B. Blocks II and III can further be combined into one block (Figure 4). Cases A and B thus differ by only one block.

A more complicated example of distinctive and significant system modification can also be analysed using Block and Boundary concept. Figure 5(c) shows a coal integrated gasification combined cycle (IGCC) system (Case C). The coal cogeneration system producing combined heat and power (CHP) can be revamped into a polygeneration system

producing methanol as an additional product to CHP (Case D), illustrated in Figure 5(d). The modified design comprises of the reuse of CO<sub>2</sub> from the flue gas of gas turbine into syngas generation via tri-reforming process, followed by methanol synthesis reaction. The design in Case D is without a capture system, hence block II is eliminated. Thus, block I in Cases C and D is almost similar, while blocks II, III and IV are distinctive in configuration.

Figure 5(e) shows the integration of syngas chemical looping system into a coal gasification plant with hydrogen production (Case E). The processes within the flowsheet have been divided into only three blocks, with no polygeneration site (block IV) in this case, according to the convention presented in Figure 4.

After defining the blocks and boundaries for processes within a system, the net energy requirement / generation and economic performances are assessed for each block. They constitute the two most essential impact criteria for integration of a particular block into a system. Since the whole purpose is to compare the performances between different flowsheets, a detailed energy and economic evaluation is not needed, provided that the parameters involved in the estimation are set on a consistent basis with valid assumptions and the results ought to achieve a satisfactory confidence level.

### *3.2.1 Shortcut Energy Auditing*

A shortcut energy auditing is undertaken to account for the energy requirement and generation by important processes within blocks that are dissimilar in configuration between various flowsheets. The energy intensity of each distinct block can thus be determined. The energy requirement and generation in the form of heat duties and power are extracted from a flowsheet. Since this is a shortcut method primarily aimed at effective screening, evaluation and decision making, the energy implication of common activities need not to be taken into

account. These include the low grade heat generation and energy requirement for coal preparation, ash and sulphur removal etc. The power requirement of ASU is 235 kWh/t O<sub>2</sub> (Armstrong et al. 2005). The steam and electricity consumption of CO<sub>2</sub> capture process (Rectisol is assumed) is 4 MJ/kmol syngas and  $5.89 \times 10^{-4}$  MWh/kmol syngas, respectively (Xie, 2001). A summary of results comparing the energy requirement and generation by each block between Cases A and B is presented in Table 2. Note that a negative sign with a net energy implies energy requirement by a block and vice versa signifies energy generation, respectively. The most crucial result in Table 2 is the difference in the net energy requirement by the CO<sub>2</sub> treatment block II+III between Cases A and B. Case B (CO<sub>2</sub> reuse into methane production) is more energy intensive than Case A (CCS) due to the CO<sub>2</sub> treatment block.

**Table 2**

Results of similar shortcut energy auditing performed on Cases C and D are presented in Table 3. The values of intermediate streams such as syngas and hydrogen exiting the boundary of a block and entering another block are not accounted, since these values would be cancelled out in the overall analysis. Block I results in a discrepancy of approximately 1.3% between Cases C and D. The CO<sub>2</sub> treatment system in Case D is more energy intensive than that in Case C, evident from the net energy requirement of 771.24 MW (block III) in Case D compared to 23.64 MW (block II+III) in Case C, respectively. Block IV in Case C generates 88% more energy compared to in Case D. However, the net product energy values need to be accounted for in the overall net energy value calculations discussed in section 3.4.

**Table 3**

Table 4 presents the energy requirement and generation of Case E. The results manifest that Case E has low energy intensities amongst all cases studied.

**Table 4**

### 3.2.2 *Shortcut Economic Evaluation*

Likewise a shortcut economic evaluation by taking the capital cost, operating cost and value of products into consideration is performed to assess the cost intensity of individual blocks within systems. The capital cost evaluation is simplified by taking the equipment cost solely into account, while the operating cost only includes the cost of raw materials (8000 operating hours per year is assumed). The costs of auxiliary equipment such as heat exchanger, mixer, splitter, pump etc. that are common in individual blocks between systems can be omitted for the purpose of comparative analysis. The costs of utility such as steam and electricity are not considered at this stage since rigorous heat integration analysis on overall systems would reveal actual utility costs. All costs of equipment are estimated using power law method (cost and size correlation) (Peters et al., 2003; Ng and Sadhukhan, 2011) and levelised to the current year value (or to a recent most consistent year) using the Chemical Engineering Plant Cost Index (CEPCI), e.g. current CEPCI = 556.8 (November 2010). The economic data are given in Appendix C. The discounted cash flow analysis is adopted to determine an annualised capital charge of 11% based on the following assumptions.

- Discount rate: 10%
- Plant life: 15 years
- Start-up period: 3 years (20%, 45%, 35%)

A shortcut economic evaluation of each block for Cases A and B is summarised in Table 5. Note that a negative economic value indicates that the product value is lower than the capital and operating costs involved and vice versa. Blocks I and IV have the same cost implications, henceforth, a comparison of economic performances between the two cases is based on the cost implication of block II+III. Clearly, the CO<sub>2</sub> treatment system (block II+III) in Case B is highly cost intensive compared to that in Case A, indicated by a TPI of 173.0

million Euro/year in Case B compared to 7.5 million Euro/year in Case A, respectively. Although methane generated as an additional product by the reuse of CO<sub>2</sub> adds 71.1 million Euro/year in Case B, it is also associated with the cost of hydrogen purchased or produced, 164.1 million Euro/year. The resulting net economic value is -101.9 million Euro/year in Case B compared to -7.5 million Euro/year in Case A, respectively.

#### **Table 5**

Table 6 provides the economic evaluation for Cases C and D. The results have shown that Case D has higher cost intensity than Case C, demonstrated by the high TPI of mainly blocks II+III and IV, under consideration. The economic value from block IV in Case D is -35.3 million Euro/year compared to 41.5 million Euro/year in Case C, respectively. The TPI of block III in Case D (403.0 million Euro/year) is 40 times higher than block II+III in Case C (9.8 million Euro/year). However, due to the higher production of high value methanol in Case D leading to an economic value of 843.7 million Euro/year compared to -9.8 million Euro/year in Case C, the option of reusing CO<sub>2</sub> seems to be more appealing than CCS. In this case, the economic value of methanol is more than the value required to offset the energy cost caused by thermodynamic infeasibility.

#### **Table 6**

The integration of chemical looping system into the coal gasification system incurs a relatively low TPI of 9.4 million Euro/year. It also results in a relatively high economic value of 82.0 million Euro/year, attributed to hydrogen generation from block II+III, presented in Table 7.

#### **Table 7**



### 3.3 Emission Balance Diagram and Emission Treatment Intensity Index Analyses

A mass and energy balance or a basic simulation model for the mass and energy balance of integrated flowsheets (e.g. in Figure 5 and discussed in Appendix A) is used to develop EBD of various cases. Figure 6(a) and (b) illustrate the EBD for Cases A (Figure 5 (a)) and B (Figure 5(b)), respectively. The removal profile in Figure 6(a) shows that a mass load of 28.2 kg/s of CO<sub>2</sub> at a mass fraction of 1.0 is removed by CO<sub>2</sub>SEP through stream 17 and transported into storage facilities. The remaining CO<sub>2</sub> is emitted from different points in the system such as exhaust gas from gas turbine etc. to the atmosphere. CO<sub>2</sub> of a mass load of 19.9 kg/s at a mass fraction of 0.59 and a mass load of 8.6 kg/s at a mass fraction of 0.18 generated from WGS and GASIFIER, respectively, primarily constitutes the generation profile. Other sources of CO<sub>2</sub> include GTCOMB and METHANOL units. The generation profile in Case B shown in Figure 6(b) is exactly the same as in Case A shown in Figure 6(a). However, the removal profile in Case B is under the generation profile that differs from Case A. This is attributed to a low mass fraction of CO<sub>2</sub> of 0.033 for a mass load of 27.1 kg/s consumed by the methanation process.

The EBD for Cases C and D are depicted in Figure 6(c) and (d), respectively. The sources of CO<sub>2</sub> generation in Case C include gasifier, high and low temperature water-gas shift reactors. A mass load of 39.4 kg/s of CO<sub>2</sub> at mass fraction of 1.0 is captured and stored whilst a mass load of 12.4 kg/s at a mass fraction of 0.1 is emitted. CO<sub>2</sub> in Case D is generated from WGS, GTCOMB, METHANOL and GASIFIER. A total of 80.4% of CO<sub>2</sub> (60.2 kg/s) is consumed by the tri-reforming reaction, while the remaining CO<sub>2</sub> is emitted from METSEP.

The EBD for Case E is depicted in Figure 6(e). CO<sub>2</sub> is generated from GASIFIER, 8.6 kg/s at a mass fraction of 0.71 and REDUCER, 43.1 kg/s at a mass fraction of 0.18. A total mass load of CO<sub>2</sub> of 51.7 kg/s at a mass fraction of 0.71 is removed and stored after being separated from FESEP.

**Figure 6**

The ETII is evaluated for Cases A-E using equation (10), 0.47, 11.19, 0.58, 8.74 and 0.38, respectively. The ETII of systems incorporating a given category of CO<sub>2</sub> disposal system must only be compared with each other because they use the same basis. In this study, two classes of CO<sub>2</sub> disposal system are considered storage system (after capture or through other concentrating processes) and reuse system (CO<sub>2</sub> is converted into other form of chemical or fuel with or without capture). Thus ETII of Case A must be compared against that of Cases C and E while the ETII of Case B should be compared against that of Case D, respectively. The longest horizontal line at the lowest mass fraction on the CO<sub>2</sub> removal profiles of Cases B and D represents CO<sub>2</sub> reuse (Figure 6(b) and (d)), while the longest horizontal line at the highest mass fraction on the CO<sub>2</sub> removal profiles of Cases A, C and E indicates CO<sub>2</sub> removal by CCS (Figure 6(a), (c) and (e)). Thus, CCS cases result in ETII of less than 1 (the removal profile is above the generation profile), whilst the reuse cases have ETII of greater than 1 (the generation profile is above the removal profile). For ETII < 1, the energy intensity of a CCS based system increases with increasing ETII (increasing ratio of area under the generation profile and area under the removal profile). In the contrary, for ETII > 1, the energy intensity of a CO<sub>2</sub> reuse system increases with decreasing ETII (decreasing ratio of area under the generation profile and area under the removal profile). From here, EBD can thus be used as an initial prediction / indicator of the treatment intensity

between these two classes of CO<sub>2</sub> disposal system (storage or reuse) based on the position of the generation and removal profiles, further discussed in section 3.4.

### *3.4 Establishing the Relationship between Emission Treatment Intensity Index and Plant Performances*

The CO<sub>2</sub> capture system and / or reuse system is expected to be integrated to coal gasification systems generating clean syngas, i.e. block I. Intuitively, there is only one way interaction from block I to block II+III+IV. This implies that any modification in block II+III+IV will not have any effect on block I. Applying the Block and Boundary concept, block II+III+IV are now grouped together and block I and block II+III+IV are analysed separately in Table 8.

#### **Table 8**

As evident, all the energy and economic criteria of block I have negligible variations between cases, once a uniform basis for the coal throughput, a heating value of 648 MW, is considered. On the other hand, the overall net energy and TPI of block II+III+IV vary depending upon ETII. The energy generation / consumption by process units has been estimated in Tables 2-4 and the resulting energy values of streams is estimated from the difference between LHV of products (methanol, acetic acid etc.) and additional feeds (e.g. hydrogen in Case B and natural gas in Case D). The overall net energy from block II+III+IV is the total energy available from process units (Tables 2-4) and streams (Table 8), on the basis of LHV of feedstock (i.e. syngas connecting block I and block II+III+IV). Similarly, TPI are given on the basis of LHV of syngas. The overall net energy and TPI are strongly dependent on ETII for block II+III+IV. As hypothesised in section 3.3, ETII should be

analysed for a given CO<sub>2</sub> disposal category. Thus, the dependency of the overall net energy and TPI on ETII must also be interpreted for a given CO<sub>2</sub> disposal category.

The overall net energy of a system implies its energy intensity. Higher the overall net energy of a system, lower is its energy intensity. The storage Cases A, C and E with  $ETII < 1$ , the overall net energy decreases (energy intensity increases) with increasing ETII (section 3.3). Thus, the sequence of cases with the highest to the lowest overall net energy is as follows: Case E > A > C (Table 8). The syngas chemical looping case is also considered as one of the CCS cases as it achieves a high level of decarbonisation (hence, high purity CO<sub>2</sub>). Analogically, the overall net energy increases with decreasing energy intensity hence increasing ETII for CO<sub>2</sub> reuse cases with  $ETII > 1$  (Case B has higher overall net energy than Case D).

TPI indicates the cost intensity of a system, i.e. higher TPI implies higher cost intensity of a system. As obvious, for storage Cases A, C and E with  $ETII < 1$ , TPI increases with increasing ETII (increasing cost intensity) (Case C > A > E) and TPI decreases with increasing ETII (decreasing cost intensity) for CO<sub>2</sub> reuse cases with  $ETII > 1$  (Case D has higher TPI than Case B).

Higher overall net energy and lower TPI of a system are desirable. This requires higher ETII in reuse case and lower ETII in storage case, respectively. For the storage cases the maximum value of  $ETII = 1$ , while for the reuse cases the minimum value of ETII is 1. Thus both cases meet at an ETII value of 1.0 (equation (9) and (10)). EBD and ETII are thus an effective way of assessing energy and economics of integrated CO<sub>2</sub> abatement systems.

#### 4. Conclusions

A shortcut methodology has been developed for analysing the performance of integrated decarbonised coal gasification systems. This methodology also serves as a decision-making tool to be conveniently used for selecting energetically and economically favourable systems at preliminary design stage. The proposed methodology comprises of two steps: preliminary screening using Gibbs energy method; this is followed by the analysis of graphical emission balance diagram (EBD) and emission treatment intensity index (ETII) for plant energy and economic performances. The relationship between ETII and plant performance is derived using shortcut energy auditing and economic evaluation aided by Block and Boundary concept on plant flowsheets. ETII applicable to individual categories of CO<sub>2</sub> disposal systems (storage or CO<sub>2</sub> reuse) is related to the energy and cost intensities of integrated CO<sub>2</sub> abatement and energy systems. Coal with CCS systems considered are: polygeneration into methanol, acetic acid, hydrogen and electricity (Case A); cogeneration into heat and electricity (Case C); and syngas chemical looping for high purity hydrogen production (Case E). Coal with CO<sub>2</sub> reuse systems under consideration include: similar polygeneration system as Case A with methanation (Case B); and tri-reforming process and methanol synthesis Case D. Amongst the CCS options, coal syngas chemical looping (Case E) is the most energy efficient and least cost intensive; this is followed by coal polygeneration with CCS (Case A); and coal cogeneration with CCS (Case C), respectively. Case D is energetically and economically more intensive than Case B.

#### Nomenclatures

A	Area under generation / removal profile on emission balance diagram
ETII	Emission Treatment Intensity Index

$\Delta G_f^\circ$	Change of Gibbs energy of formation
$\Delta H_f^\circ$	Standard enthalpy change of formation
$\Delta H_R^\circ$	Standard enthalpy change of reaction
$l_j$	Mass load of CO <sub>2</sub> within a step $j$
$m_k$	Mass load of CO <sub>2</sub> within a step $k$
$M$	Total mass load of CO <sub>2</sub> shown as the final point on the profile
$n$	Number of moles
$R$	Universal gas constant
$T$	Temperature
TPI	Total plant investment
$U$	Total number of steps in the generation profile
$W$	Total number of steps in the removal profile
$\alpha$	Mass fraction of CO <sub>2</sub> in the generation profile
$\lambda_j$	Function of generation profile with steps $j$
$\mu_k$	Function of removal profile with steps $k$
$\omega$	Mass fraction of CO <sub>2</sub> in the removal profile

## Appendix A

Process descriptions for Cases A-E are provided as follows:

### Case A-Coal polygeneration with CCS (Figure 5(a))

Electricity, hydrogen, methanol and acetic acid are the products generated from this polygeneration system. Coal-water slurry is gasified (GASIFIER) using oxygen-enriched air as the gasification medium to produce syngas (stream 3), containing a mixture of H<sub>2</sub>, CO,

CO<sub>2</sub>, H<sub>2</sub>O as major components. Subsequently, the syngas is cooled in a syngas cooler (SYNGCOOL), and undergoes a series of gas conditioning and cleaning processes, comprising ash removal in CYCLONE, water removal (H2OREM), H<sub>2</sub>S removal (H2SREM) and CO<sub>2</sub> separation (CO2SEP) processes. A target stoichiometric ratio of (H<sub>2</sub>-CO<sub>2</sub>) / (CO+CO<sub>2</sub>) = 2 of syngas for methanol synthesis (METHANOL) is attained (Ng and Sadhukhan, 2011). A flash column (METSEP) is used to separate the gaseous and liquid products. The offgas containing unreacted gases such as H<sub>2</sub>, CO, CH<sub>4</sub> etc. (stream 21) is utilised in power generation through gas turbine (GASTURB) and acetic acid (ACEREACTION) production. Hydrogen is separated via H<sub>2</sub>/CO separation process (H2COSEP) as a product. Liquid methanol (stream 22) is sent to distillation units (METDISTL) to further recover methanol coming from METSEP. A portion of the liquid methanol (stream 35), depending on the availability of CO in the offgas after separation from the product gas, is used in acetic acid synthesis.

#### Case B-Coal polygeneration with CO<sub>2</sub> methanation (Figure 5(b))

Electricity, methanol, acetic acid and methane are the products generated from this polygeneration system. This case only differs from Case A in terms of the CO<sub>2</sub> disposal step. In this case, CO<sub>2</sub> is reused into methane production in METHANAT through Sabatier's reaction, instead of storage in Case A. All the hydrogen produced from the system is utilised in methane production and a part of the hydrogen required by the process is imported.

#### Case C-Coal IGCC with CCS (Figure 5(c))

The main products from this cogeneration system are heat and electricity. In this case, coal is gasified into syngas for the production of heat and power. The syngas is conditioned through high and low temperature water-gas shift reactors (HTWGS and LTWGS) and is

cleaned through H<sub>2</sub>S removal (H<sub>2</sub>SREM) and CO<sub>2</sub> removal (CO<sub>2</sub>SEP). CO<sub>2</sub> is captured and stored. The clean syngas is then used into gas turbine (GASTURB) for the generation of electricity.

Case D-Coal IGCC with tri-reforming and methanol synthesis (Figure 5(d))

Methanol and electricity are the main products from this system. Case D is a modification of Case C. In Case D, CO<sub>2</sub> in the exhaust gas (EXHGAS) from gas turbine (GASTURB) is reused in tri-reforming process (TRIREFOR) for the production of methanol. Tri-reforming of methane (Song and Pan, 2004) uses CO<sub>2</sub>, steam and oxygen for the production of valuable syngas with desired ratio and for the reduction of carbon formation on catalyst. Hydrogen (stream 15) is separated from the syngas from gasification using pressure swing adsorption (PSA). Hydrogen recovered is then combined with the syngas from tri-reforming process (stream 26). The remaining CO enriched gas (stream 14) from PSA is sent to gas turbine for electricity generation. A highly concentrated CO<sub>2</sub> stream is resulted from gas turbine combustion. The exhaust gas from gas turbine (EXHGAS) is then routed to the tri-reforming process. The unreacted offgas (stream 36) from methanol synthesis are recycled to enhance the production of methanol, while the rest is purged (stream 35). The proposed integrated system meets the desired H<sub>2</sub>/CO molar stoichiometric ratio in the feed gas to the methanol synthesis without any use of CCS.

Scheme E-Coal syngas chemical looping (Figure 5(e))

Hydrogen is the sole product from this system. Syngas is generated in the same way as in all other cases. Case E considers the integration of syngas chemical looping concept into a coal gasification system, with an aim of producing high purity CO<sub>2</sub> (REDUCER) and



hydrogen (OXIDISER) simultaneously. The metal oxide ( $\text{Fe}_2\text{O}_3$ ) can be recovered through combustor (COMBUST) using air, and recycled back to REDUCER.

The syngas chemical looping concept (Tomlinson et al., 2007; Fan et al., 2008) is featured in Figure A.1. Firstly, the syngas generated from gasifier consisting of  $\text{CO}$ ,  $\text{H}_2$  and light hydrocarbons is introduced into a reducer, where it is reacted with  $\text{Fe}_2\text{O}_3$ .  $\text{Fe}_2\text{O}_3$  is reduced to form  $\text{Fe}$  during the reaction, whilst  $\text{CO}_2$  and  $\text{H}_2\text{O}$  are the main products formed according to equations (A.1) and (A.2). Equation (A.3) presents the generic reaction applicable to  $\text{CO}$ ,  $\text{H}_2$  as well as other hydrocarbons, occurring in the reducer.  $\text{MO}$  and  $\text{M}$  represent different metal oxide phases. In the next stage,  $\text{Fe}$  is reacted with steam to produce  $\text{H}_2$  (equation (A.4)), while  $\text{Fe}$  is oxidised to  $\text{Fe}_3\text{O}_4$ . Finally,  $\text{Fe}_3\text{O}_4$  is regenerated into  $\text{Fe}_2\text{O}_3$  via combustion with air and recycled back to the reducer, provided in equation (A.5).

Reducer: (Tomlinson et al. 2007)



Oxidiser: (Tomlinson et al. 2007)



Combustor: (Tomlinson et al. 2007)



**Figure A.1**

## **Appendix B**

The thermodynamic data (Atkins and Paula, 2005) required for estimating the standard enthalpy change of reaction and standard Gibbs energy of reaction is provided in Table B.1.

### **Table B.1**

## **Appendix C**

The economic data (Hamelinck and Faaij, 2002; Denton, 2003; IPCC, 2005; Larson et al., 2005; Stiegel and Ramezan, 2006; Zhu and Jones, 2009; DECC, 2010; ICIS Pricing, 2010; Methanex, 2011) required for evaluating capital cost, operating cost and value of products are provided in Table C.1.

### **Table C.1**

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