

# CO<sub>2</sub> Abatement Strategies for Polygeneration Systems: Process Integration and Analysis

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## Abstract

Several decarbonised polygeneration systems exploiting carbon capture and storage (CCS) or CO<sub>2</sub> reuse technologies for the conversion of primary resources into clean fuels, chemicals, electricity and heat are systematically analysed for techno-economic feasibility. A process simulation, energy integration and economic analysis based approach has been employed to arrive at a representative set of performance indicators for the trade-off analysis of polygeneration systems. These indicators include the effect of process configurations and operating conditions on the economic potential (*EP*), energy efficiency, decarbonisation potential, economic risks, value of products and sensitivity in *EP* due to carbon taxations. The systems under consideration include coal gasification systems with cogeneration and polygeneration, integrated with various CO<sub>2</sub> abatement systems. Transforming a CCS based polygeneration Scheme A producing electricity, hydrogen, acetic acid and methanol, into an equivalent Scheme B additionally producing methane from the captured CO<sub>2</sub> does not necessarily enhance efficiency, economic and emission performances. Upgrading cogeneration Scheme C into a polygeneration Scheme D additionally producing methanol clearly improves all performance indicators. While bio-oil based polygeneration system (Scheme E) creates environmental incentives, its economic competitiveness is uncertain and can be enhanced by introducing credits on product prices. Promising results in terms of improved energy efficiency from 36% in IGCC with CCS scheme to above 70% in

polygeneration schemes, viable *EP* and a minimum of 75% of plant-wide CO<sub>2</sub> emission reduction demonstrate that the polygeneration Schemes A, D and E can become low carbon technologies of choice.

*Keywords:* chemical and transportation fuel production; CO<sub>2</sub> reuse, recycling and carbon capture and storage; clean coal technology; bioenergy and biorefinery; low carbon energy, low carbon technology roadmap; hydrogen, methanol, acetic acid and methane production from power plant expansion.

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## **1. Introduction**

Dwindling global oil reserves, environmental concerns and the need for energy security have generated strong research and development focus in clean coal, natural gas and biomass polygeneration technologies, producing transportation fuels, chemicals, heat and electricity. Polygeneration systems incorporating CCS and CO<sub>2</sub> recycling and reuse technologies provide low plant emission, enhanced and flexible switching capability between a diverse range of feedstocks and products and thus providing security of supply and economic drives (Li et al., 2010; Macdowell et al., 2010; Adams and Barton, 2011; Pires et al., 2011). Amongst various fossil resources and technologies, coal with CCS has been recognised to make a significant contribution to the increasing demand for electricity (Ng et al., 2010). The ScottishPower (2008) has engaged into a demonstration project that uses Scottish coal and biomass co-firing technology integrated with advanced CCS options. A large scale co-processing plant planned in Scotland is an example of UK's energy security goals. However, considering the uncertainty in storing CO<sub>2</sub>, its recycling and reuse for chemical production has started to receive high priorities in some regions, US, Denmark, Australia, etc. (Rihko-Struckmann et al., 2010). CO<sub>2</sub> can be reused for enhanced oil recovery in oil

extraction process; microalgae production; production of urea, methanol, dimethyl ether, Fischer-Tropsch liquids, methane (Sabatier's reaction), syngas (tri-reforming process) and hydrogen (Song and Pan, 2004; Li et al., 2006; Barbarossa et al., 2009; Rihko-Struckmann et al., 2010). A recent breakthrough in the area of CO<sub>2</sub> reuse is the launching of the George Olah Plant in Iceland in 2010, for the production of methanol from captured CO<sub>2</sub> from industrial flue gases (CRI, 2010). Further, the Annex I countries have realised that switching to fossil resources with CCS or CO<sub>2</sub> reuse alone cannot bring in the carbon saving needed to restrict the temperature rise up to below 2-3°C over this century and their exploitation must be in combination with biomass feedstocks. The Non-Annex I countries have also committed towards adaptation to alternative technologies to combat against climate change (UNFCCC, 2010). Thus, in parallel to CCS and CO<sub>2</sub> reuse technologies, lignocellulosic biomass must be co-processed for achieving realistic carbon reduction. Bio-oil, a higher energy density liquid, from biomass fast pyrolysis processes can be converted to methanol or liquid transportation fuels (diesel and gasoline) (Bridgwater, 2009; Venderbosch and Prins, 2010; Ng and Sadhukhan, 2011a, 2011b; Sadhukhan and Ng, 2011). This study further looks into the creation of polygeneration flowsheet options incorporating gasification of coal and bio-oil, alternative CO<sub>2</sub> abatement technologies and creating a whole range of processing-production possibilities.

**Error! Reference source not found.** provides overall integrated and cleaner polygeneration schemes with gasification and carbon capture technology as well as CO<sub>2</sub> reuse strategies. The CCS and with CO<sub>2</sub> pre-combustion capture (Scheme A) and reuse in methane synthesis by Sabatier's reaction (Scheme B) are proposed to produce methanol, acetic acid, electricity and hydrogen. Scheme C includes the coal IGCC system with CCS. In Scheme D, post-combustion CO<sub>2</sub> from gas turbine (after hydrogen recovery) is tri-reformed using natural gas. The product gas from tri-reforming is conditioned by the addition of recovered hydrogen for the synthesis of methanol.

Considering the co-processing potential of bio-oil in Scheme A, the Scheme E similar to Scheme A is evaluated for bio-oil as a feedstock. The products and processes selected are representative, exploiting process integration and conditional synergies, for comparative analysis between polygeneration systems exploiting CCS and / or CO<sub>2</sub> reuse.

Figure 1 Further, there are clear and strengthening imperatives for adopting process integration strategies, otherwise undermined subject, for developing sustainable polygeneration systems. This work takes a systematic process integration approach using heat integration (Smith, 2005), value analysis (Sadhukhan et al., 2004; Sadhukhan et al., 2008), biorefinery systems synthesis (Kokossis and Yang, 2010) and systems methodologies for CCS design (MacDowell et al., 2010) etc., for enhancing overall energy and decarbonisation efficiencies. Adams and Barton (2011) have addressed systems questions such as how a rising CO<sub>2</sub> tax incentivises the production of more liquid fuels instead of electricity due to the tax implication on the latter product. The study by Rihko-Struckmann et al. (2010) evaluated the thermodynamic limitations, the energy and exergy efficiencies of a number of CO<sub>2</sub> usage routes for the storage of electrical energy into chemicals. Studies by Ng and Sadhukhan (2011a, 2011b) and Sadhukhan and Ng (2011) have demonstrated comprehensive techno-economic performance analyses of a number of bio-oil based biofuel platforms, utilising indirect gasification route or direct upgrading route, for the production of methanol, Fischer-Tropsch liquids, gasoline and diesel alongside heat and electricity. Venderbosch and Prins (2010) have studied characterisation of functionalities and chemical constituents of bio-oils based on target chemicals and biofuels to be generated. Their approach includes efficient heat integration, control and reliability analysis of a number of pyrolysis reactors, e.g. fluid bed, rotating cone and vacuum pyrolysis at a demonstration scale and ablative and twin screw at a pilot scale, for the production and characterisation of bio-oils.

The current study draws on the above analysis to identify systems internal and external variables to propose effective, integrated production planning and process operation strategies, considering a wide range of market price fluctuation and implication of the emission trading scheme and taxation (Postnote, 2010). With the recognition that industrialisation will even be at a faster pace, the process integration tools, built upon basic principles of the most efficient use of raw materials, energy and capital, would be fundamental to the design of fully integrated environmentally and economically sustainable polygeneration technologies. The process integration tools have been applied for optimal utilisation of internal and external opportunities and to suggest appropriate indicators for polygeneration systems trade-off analyses. These performance indicators include the effect of process configurations and operating conditions on the economic potential (*EP*), plant-wide decarbonisation potential, economic risks, product values and sensitivity in *EP* due to carbon taxations, discussed in the methodology in Section 2. Further, the case studies effectively demonstrate whether there is any room for improvement in a highly capital and energy intensive polygeneration system, such as inserting an additional production pathway through CO<sub>2</sub> reuse while eliminating the need for a CO<sub>2</sub> storage system; the effect of revamping a cogeneration system into a polygeneration system through CO<sub>2</sub> reuse while eliminating the need for a CO<sub>2</sub> capture system; comparative performances between fossil and biomass based polygeneration systems, in Section 3.

## **2. Methodology**

The methodology in Figure 2 comprises of:

1. *Process simulation in section 2.1.* Process configurations and operating conditions were selected based on scaled up and industrially relevant values. In addition, the generation of flowsheets embraced various logical, cost-effective and energy efficient modifications. ASPEN Plus simulation has been adopted to model the processes, e.g. Gibbs reaction

modelling for gasifier; equilibrium reaction modelling for water-gas shift, methanol synthesis, acetic acid synthesis and tri-reforming reactors. Validation of the gasifier model – the core part of the systems has been undertaken against literature results.

2. *Energy integration in section 2.2.* Systematic energy integration through data extraction, screening and classification of heat integration task, composite curve analysis, CHP network design and heat and power balance has been performed on the systems to attain high energy efficiency.
3. *Economic evaluation in section 2.3.* Comprehensive economic analysis framework using economic potential as the indicator has been established, which comprises the evaluation of capital and operating costs as well as the product costs. Other assessment includes the analysis of production portfolio and process operations for minimising the economic risk due to price fluctuation of products, through a classification by chances of occurrence.

Final analysis is done by the comparison of energy efficiency, economic and emission performances between cases under consideration in order to derive the technological preferences. The impact of and sensitivity to the carbon tax on the economics of the systems has also been another criterion for technology ranking.

A selection of five case studies with schemes shown in **Error! Reference source not found.** based on the criteria discussed in the introduction has been carried out using the proposed methodology. Scheme A with coal polygeneration and CCS is presented in detail to explain the methodology (sections 2.1-2.3).

**Figure 2**

## 2.1 Process Simulation

Scheme A processing 2000 t/d of coal into methanol, acetic acid, electricity and hydrogen is simulated in ASPEN Plus, using Non-Random Two-Liquid (NRTL) property method. The simulation results are illustrated in Figure 3. The basis of modelling the process units is summarised in Table 1.

### **Figure 3**

### **Table 1**

The coal-water slurry is gasified at 75 bar and 1371°C in entrained flow gasifier (GASIFIER), using oxygen-enriched air (93.4% O<sub>2</sub>, 1% N<sub>2</sub> and 5.6% Ar) as the gasification medium. The coal-water slurry and oxygen-enriched air are preheated to 121°C and 83°C, respectively prior to gasification. The coal gasification model validated against literature results (Larson and Tingjin, 2003) is used in this study. The product gas (stream 3), containing a mixture of H<sub>2</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O as major components with H<sub>2</sub>/CO molar ratio of 0.7 is cooled down to 430°C in SYNGCOOL, followed by ash removal in CYCLONE. The gas is further expanded in SYNGEXP in order to meet the operating conditions of water-gas shift (WGS) reaction, i.e. 25 bar and 250°C. The outlet temperature of the product gas from SYNGCOOL, operating conditions of WGS and the steam requirement by WGS are decided to achieve desired H<sub>2</sub>/CO molar ratio of 2.1 in the product gas. Furthermore, numerous gas clean-up steps such as water (H2OREM), H<sub>2</sub>S (H2SREM) and Rectisol process (Xie, 2001) for CO<sub>2</sub> removal (CO2SEP) processes are deployed to attain a target stoichiometric ratio of  $(H_2 - CO_2) / (CO + CO_2) = 2.07$  of the gas for methanol production (Ng and Sadhukhan, 2011a).

The clean product gas is compressed to 100 bar (SYNGCOMP) to meet the high operating pressure requirement by the methanol synthesis reactor (METHANOL). The methanol synthesis reactions in equations (1)-(3) take place in gaseous phase at 100 bar and 250°C (Hamelinck and

Faaij, 2002), with a CO conversion of 75%. The gaseous product from METHANOL is expanded to 24 bar in METGEXP. A flash column (METSEP) is further used to separate the gaseous and liquid products at 40°C and 24 bar. 98% recovery (molar basis) of methanol from liquid stream 22 from METSEP is attained. 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. The offgas distribution can be adjusted through sensitivity analysis, discussed in section 2.3.1.



Hydrogen is separated via a H<sub>2</sub>/CO separation process (H<sub>2</sub>COSEP), such as cryogenic separation (technology developer such as Linde), e.g. partial condensation and liquid methane wash (Gunardson, 1998). Liquid methanol is sent to distillation units (METDISTL) to further recover 99.5% of methanol coming from METSEP (Uhde, 2008). A portion of the liquid methanol, depending on the availability of CO in the offgas after separation from the product gas, is used in acetic acid synthesis. The primary acetic acid synthesis route is via methanol carbonylation (equation (4)) at 150°C and 30 bar (Yoneda et al., 2001). This process technology is available from BP, Monsanto, Chiyoda and UOP.



Three main products obtained are hydrogen (54.5 t/d, 75.7 MW, stream H<sub>2</sub>), acetic acid (583.7 t/d, 88.5 MW, stream ACOH) and methanol (716.2 t/d, 166.6 MW, stream MEOH). The site has a net deficit of power of 14.4 MW, even though the gas turbine produces 2.6 MW of power.

Additional power can be generated through combined heat and power (CHP) production followed by heat recovery from SYNGCOOL, heat recovery steam generator (HRSG) and reactors' cooling units, analysed in section 2.2.

## *2.2 Heat Integration and CHP Network Design*

A systematic heat integration methodology and CHP network design for the recovery of maximum heat and power as a product enhancing the energy efficiency of an overall system is presented in **Error! Reference source not found.** The design procedures encompass the fundamental pinch analysis for heat exchanger network design and a series of heuristic and experience based methodology for classifying the level of heat within the system. The design procedures have the advantage of generating the layout of a reasonably high efficiency CHP system in a systematic manner, detailed in previous publication by Ng et al., 2010.

### **Figure 4**

Important data such as temperature and heat duties across process units are extracted from ASPEN Plus flowsheet simulation results in **Error! Reference source not found.**, for screening and classification in high and low level heat integration tasks. The heat supply and demand of individual units are categorised in high and low level tasks based on the temperature levels and the amount of heat duties. The high level tasks involve CHP network design for steam generation and consumption based on composite curve and energy balance analyses, whilst the low level tasks indicate process-to-process heat exchanger network design based on pinch analysis (Smith, 2005; Ng et al., 2010). The low grade heat utilisation into hot water generation is also considered in heat exchanger network design.

The results of data extraction and classification of heat integration tasks in Scheme A (Figure 3) are summarised in **Error! Reference source not found.** and discussed as follows.

*Low level task:* The heat from HRSG (3312 MW) though available at high temperature range (742°C-100°C) is negligible for steam generation (< 1 kg/s steam) and thus it is used for hot water generation, very relevant in the UK context. The heat demands by HE1, HE2 and HE5 at low temperature ranges are satisfied by the sensible heat available in H2OREM. The demand for LP steam (5 bar) is 4 MJ/kmol syngas by Rectisol (Xie, 2001) and 0.45 t/t methanol by METDISTL process (Uhde, 2008), respectively.

*High level task:* The MP steam (14 bar) required by WGS is determined based on desired output condition of the product gas. Three levels of steam mains are considered according to the system requirement: VHP (80 bar, superheated to 500°C) that can be generated utilising exothermic heat of reaction from GASIFIER and sensible cooling duty of SYNGCOOL, MP (14 bar, superheated to 230°C) (sources are METHANOL and WGS reactors) and LP (5 bar and 152°C). It can be noted that the modelling of GASIFIER as RGibbs reactor (Table 1) may adequately present the product gas composition (Larson and Tingjin, 2003), but predict an optimistic amount of exothermic heat of reaction due to the consideration of coal analysis at an elemental level. Therefore, Tables 2-3 highlight only the useful heat obtainable from GASIFIER, compared to the value presented in simulation Figure 3.

## **Table 2**

*Heat and power balances:* Following the systematic screening and classification of high level and low level heat integration tasks the amounts of steam generation, process to process heat recovery and hot water recovery are decided. The heat sources (SYNGCOOL, GASIFIER, WGS and METHANOL) provide steam to the steam mains and the heat sinks (WGS, Rectisol and METDISTL) consume steam from the steam mains. The remaining steam is expanded through steam turbines (ST1, ST2 and ST3) for power generation. For the maximum amount of steam generation at the required levels from the heat sources, a minimum temperature approach of 20°C

between the heat of reactions or sensible heats available and the steam to be generated is maintained and can be explained through composite curve analysis in the form of temperature driving force (y axis) vs enthalpy (x axis) diagrams, between the heat sources and heat sinks. The steam consumptions by heat sinks and the power demands by relevant units are estimated using the literature value as aforementioned or energy balances simulated in ASPEN Plus. The resulting steam generation - distribution and power balances are presented in CHP network diagram in **Error!**

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### **Figure 5**

The heat and power balance of the overall system is presented in **Error! Reference source not found..** The power requirements by the air separation unit (ASU) and the Rectisol unit are 235 kWh/t O<sub>2</sub> (Armstrong et al., 2005) and  $5.89 \times 10^{-4}$  MWh/kmol syngas (Xie, 2001), respectively. The net power generation is enhanced from a deficit of 14.4 MW previously obtained from process simulation in section 2.1 to 177 MW after heat integration. As a result, the net energy efficiency is increased to 78%, based on 648 MW of LHV of coal. This is in comparison to only 36% of energy efficiency achievable from a coal IGCC plant with CCS (Scheme C) under consideration (NETL, 2010). The net energy efficiency is defined as the sum of LHV of all the products divided by the sum of LHV of all the feedstocks.

### **Table 3**

## *2.3 Economic Analysis*

The economic analysis of decarbonised polygeneration systems and the sensitivity analyses of the offgas distribution and conversion to methanol synthesis on the overall system performance are presented in section 2.3.1. The sensitivity analysis of price fluctuation of products is included in section 2.3.2.

### 2.3.1 Economic Potential (EP) Analysis

EP of polygeneration systems is determined using equation (5).

$$EP = H \sum_{i=1}^{i=NP} r_i p_i - CC - OC \quad (5)$$

$H$  is the total number of operating hours per year;  $r_i$  and  $p_i$  are the production rate and unit price of product  $i$ , respectively;  $NP$  is the total number of products;  $CC$  and  $OC$  are annual capital cost and annual operating cost, respectively.

The capital cost is evaluated in terms of the direct (ISBL and OSBL) and indirect capital costs. The ISBL comprises the cost of equipment which can be estimated using cost and size correlation, in equation (6). The parameters such as base cost, base scale and scale factor  $\theta$  (Hamelinck and Faaij, 2002; Denton, 2003; IPCC, 2005; Larson et al., 2005; Zhu and Jones, 2009) are given in Appendix A. Each cost is levelised to the current cost using equation (7), where Chemical Engineering Plant Cost Index (CEPCI) is applied. The parameters for the estimation of the OSBL and the indirect capital cost (Hamelinck and Faaij, 2002) are also provided in Appendix A. The discounted cash flow method is applied for determining the annual charge for the capital investment, i.e. 11% using the following assumptions:

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

$$\frac{COST_{size2}}{COST_{size1}} = \left( \frac{SIZE_2}{SIZE_1} \right)^\theta \quad (6)$$

$SIZE_1$  and  $COST_{size1}$  represent the capacity and the cost of a base unit, whilst  $SIZE_2$  and  $COST_{size2}$  represent the capacity and the cost of the unit after scaling up/down, respectively.

$$\text{Present cost} = \text{Original cost} \times \left( \frac{\text{Index at present}}{\text{Index when original cost was obtained}} \right) \quad (7)$$

The operating cost comprising of the fixed and variable costs is evaluated. The parameters for estimating the operating costs (Tijmensen et al., 2002; Sinnott, 2006; DECC, 2010) are given in Appendix A. The economic assumptions are as follows:

- Operating hours per year ( $H$ ): 8000 hours
- Current CEPCI: 555.2 (April, 2010)

The current market prices / estimated cost of production are identified for evaluating the total value of the products, i.e. electricity (74.14 Euro/MWh (DECC, 2010)), hydrogen (1104 Euro/t (Stiegel and Ramezan, 2006)), acetic acid (550 Euro/t (ICIS Pricing, 2010)) and methanol (255 Euro/t (Methanex, 2010)).

The offgas from methanol synthesis reaction can be distributed into electricity, hydrogen and acetic acid production. The effect of split fractions of 0.9, 0.5 and 0.1 of stream 28 in Figure 3 on overall  $EP$  prior to the heat integration is presented in Table 4(a). A split fraction of 0.9 means 90% of the offgas is used for hydrogen and acetic acid production while 10% is used for power generation through gas turbine. The scenario with a split fraction of 0.9 is the most economically favourable case,  $EP = 33.7$  million Euro/y. The other two scenarios with split fractions of 0.5 ( $EP = -6.6$  million Euro/y) and 0.1 ( $EP = -46.8$  million Euro/y) are not economically viable. There is no net electricity generation from all these scenarios. Lowering the split fraction of the offgas from 0.9 to 0.1 increases the electricity generation from the gas turbine. This in turn reduces the plant's operating cost by 10%. However, the value of products is reduced significantly by 87% due to the reduction in the split fraction. Thus, overall a higher level of diversion into added value production

is desired. High added value production is however accompanied with a higher level of economic risk, discussed in section 2.3.2.

Two different values of conversion of CO in methanol synthesis, 75% and 50%, after heat integration and for an offgas split fraction of 0.9, producing 43.7 t/h and 28 t/h of methanol, respectively, are also taken into consideration to select preferred operating scenario in terms of *EP* (Table 4(b)). The trends suggest that lower conversion of CO in methanol synthesis reaction results in higher *EP*, 211.7 million Euro/y at 50% conversion and 139.9 million Euro/y at 75% conversion, respectively. This is primarily due to the higher value acetic acid production, 49.9 t/h at 50% conversion compared to 24.3 t/h at 75% conversion, respectively. A portion of methanol, 27.1 t/h for 50% conversion and 13.8 t/h for 75% conversion, respectively is utilised in carbonylation process for the formation of acetic acid (equation (4)).

The sensitivity studies of the distribution of the offgas from the methanol synthesis reactor as well as the conversion in methanol synthesis reaction explain the importance of manipulation of operating conditions on polygeneration system performance. The manipulation of these operating conditions serves as a low cost modification option for the mitigation of moderate level of economic risks, discussed in section 2.3.2. The increased *EP* presented in Table 4(a) and (b) also demonstrates the importance of energy integration and efficiency studies. The power generating from gas and steam turbines is sufficient for the whole system supply, leading to a considerable reduction in operating cost by 19% and an increase in product value by 56%.

#### **Table 4**

##### *2.3.2 Sensitivity Analysis of Price Fluctuation of Polygeneration Products*

Uncertainty in price of chemicals is due to instability in supply and demand, oil prices and unforeseen circumstances such as natural disaster and oil spill etc. Further complication arises

particularly in a polygeneration plant wherein there are competing productions. Therefore, the effect of price fluctuations of products on  $EP$ , through classification by chances of occurrence has been introduced as follows.

There are four products under consideration: electricity, hydrogen, acetic acid and methanol. The unit prices of products,  $p_w, p_x, p_y$  and  $p_z$ , respectively, are considered as variables. Three sets of prices are assumed for each product: base price ( $p_{i,0}$ ), a price lower than the base price by a difference of  $\Delta\%$  ( $p_{i,-\Delta\%}$ ) and a price higher than the base price by a difference of  $\Delta\%$  ( $p_{i,+\Delta\%}$ ). Based on Counting Principle, there are 81 ( $n$ ) combinations due to three sets of prices for four individual products ( $3 \times 3 \times 3 \times 3$ ), (equation (8)).

$$\begin{bmatrix} p_{w,0} & p_{x,0} & p_{y,0} & p_{z,0} \\ p_{w,-\Delta\%} & p_{x,-\Delta\%} & p_{y,-\Delta\%} & p_{z,-\Delta\%} \\ p_{w,+\Delta\%} & p_{x,+\Delta\%} & p_{y,+\Delta\%} & p_{z,+\Delta\%} \\ \vdots & \vdots & \vdots & \vdots \end{bmatrix}_{n \times 4} \begin{bmatrix} r_w \\ r_x \\ r_y \\ r_z \end{bmatrix}_{4 \times 1} = \begin{bmatrix} r_w p_{w,0} + r_x p_{x,0} + r_y p_{y,0} + r_z p_{z,0} \\ r_w p_{w,-\Delta\%} + r_x p_{x,-\Delta\%} + r_y p_{y,-\Delta\%} + r_z p_{z,-\Delta\%} \\ r_w p_{w,+\Delta\%} + r_x p_{x,+\Delta\%} + r_y p_{y,+\Delta\%} + r_z p_{z,+\Delta\%} \\ \vdots \end{bmatrix}_{n \times 1} \quad (8)$$

The  $EP$  (equation (5)) due to the market price combinations for a constant  $\Delta\%$  and variable  $\Delta\%$  in equation (8) is predicted in Matlab environment. The  $CC$  and  $OC$  are 85.7 million Euro/y and 67.4 million Euro/y, respectively. The value of products and  $EP$  of the base case in Figure 3 on a basis of 8000 operating hours per year are 293.0 million Euro/y and 139.9 million Euro/y, respectively (Table 4(b)). By assuming that the system results in an acceptable  $EP$  at the current market scenario, any variation in  $EP$  due to price fluctuation may lead to an economic risk. An “economic risk” refers to a loss in revenue due to any event (a combination of product prices). It is important to predict and classify the potential economic risk in various ranges, e.g.  $\geq 0\%$ ,  $0\%$  to  $-20\%$ ,  $-20\%$  to  $-50\%$  and  $< -50\%$  ( $-$  indicates reduction in revenue compared to the base case revenue). The frequency of having a particular class of economic risk (e.g.  $\geq 0\%$ ) is determined by counting the number of events resulted into the given class of economic risk. The probability of

occurrence of a particular class of economic risk is obtained by the ratio of the frequency of events resulting into the given class of economic risk to the total number of events.

Case 1: Constant  $\Delta\%$

Table 5(a) summarises the classification of economic risks, the frequency of events resulting into each class of economic risk, probability of occurrence of each event and the decision to be taken, based on 50% variation in individual product price fluctuation. All scenarios with positive variation in *EP* are in safe *EP* region, and the probability of having such scenario is approximately 51%. Thus, the probability of having moderate to critical economic risk is significant.

Case 2: Variable  $\Delta\%$

Table 5(b) takes account of individual product price fluctuations over a certain period discussed as follows, in order to assess the economic risk, frequency of events within each class of economic risk, probability of occurrence of each event and the modification requirement.

**Table 5**

The contract price of methanol from January 2006 to September 2010 (Methanex, 2010) is presented in Figure 6(a). The price fluctuation of acetic acid is not published, and thus the price fluctuation of methanol is used as a benchmark for its price. The price of hydrogen is often kept proprietarily by organisation. The price fluctuation of hydrogen is thus inferred from the price of natural gas (DECC, 2010) (Figure 6(b)). The price of electricity (Figure 6(b)) is also obtained from DECC (2010). Table 6 presents the percentage price variation from the base case unit price of products.

**Figure 6**

**Table 6**

It is evident that 41 events in case of constant  $\Delta\%$  and 52 events in case of variable  $\Delta\%$  out of a total of 81 events (combinations of prices) result in higher *EP* or no economic risk. Table 5(b) indicates 64% probability of having no economic risk and 7% probability of having critical economic risk. However, the probability of having moderate to high economic risks is also within a range of 28% and comparable to 32% probability in the constant  $\Delta\%$  case. This suggests that a significant reduction in revenue due to product price fluctuation may be encountered, and hence, various levels of cost modification strategies must be analysed as a part of detailed system design exercise. To mitigate moderate to high economic risk, the low to high cost modification in Table 5 may be achieved by diversion to lower impact (generally lower value) products (e.g. by the manipulation of operating conditions) discussed in section 2.3.1, while the critical economic risk may only be mitigated by plant retrofitting. The product with the highest market price fluctuation is likely to result in the highest economic risk and vice versa. Thus the sequence of the highest to the lowest impact products (or the reverse order of preference in terms of product diversion) in Table 6 is as follows, acetic acid / methanol > hydrogen > electricity. Polygeneration framework provides flexibility in product diversion and thereby ways of mitigating various levels of economic risks.

### **3. CO<sub>2</sub> Emission Minimisation through Process Modification**

The simulation of other polygeneration schemes is outlined in section 3.1. The thermodynamic efficiency, *EP* and environmental impact of the various process schemes are presented in section 3.2. The CO<sub>2</sub> mitigation options and future deployment potential of polygeneration systems are discussed in section 3.3.

#### *3.1 Simulation of Polygeneration Schemes*

All schemes, A-E, under consideration have the same coal or bio-oil input processing capacity, i.e. 648 MW. Schemes A-D have a throughput of 2000 t/d of coal, while 3102 t/d of bio-

oil is used in Scheme E to achieve 648 MW (LHV of bio-oil is 18 MJ/kg). Additional operating parameters of Schemes C-E used in ASPEN Plus simulation are given in Appendix B. Heat integration strategy illustrated in **Error! Reference source not found.** is undertaken for all systems under consideration.

Scheme B-Coal polygeneration with CO<sub>2</sub> methanation (Error! Reference source not found.(b))

CCS is included in Scheme A in order (i) to obtain a suitable stoichiometric ratio in the product gas for methanol production; (ii) to reduce CO<sub>2</sub> emission from the system. Whilst carbon capture unit is essential, storage is optional, however. CO<sub>2</sub> captured can be utilised into other chemical production, such as methane, benzene, methanol etc. An alternative process Scheme B that utilises CO<sub>2</sub> into methane production in Sabatier's reaction (equation (9)) is introduced. The operating condition of the Sabatier's reaction is set at 2 bar and 300°C (Barbarossa et al., 2009). 2.56 kmol/s of hydrogen is required and 96% conversion of CO<sub>2</sub> by mole is achieved for the production of 35.5 t/h of methane. CO<sub>2</sub> is released with the exhaust gas from gas turbine and unreacted gases from acetic acid synthesis and Sabatier's reactions. The Sabatier's reaction has been successful in space-based applications. These include production of water in International Space Station and the In-Situ Resource Utilisation for space exploration to Mars by NASA (Curie, 2010).



Scheme C-Coal IGCC with CCS (Error! Reference source not found.(c))

In this scheme, coal is gasified into syngas and heat and power, with CCS in pre-combustion process (Ng et al., 2010). CO<sub>2</sub> may be emitted with the exhaust gas from the gas turbine.

Scheme D-Coal IGCC with tri-reforming and methanol synthesis (Error! Reference source not found.(d))

The cost of CCS and the degree of decarbonisation pose an important trade-off in coal IGCC system with CCS (Ng et al., 2010). Scheme D producing methanol by the reuse of CO<sub>2</sub> generated from the gas turbine in tri-reforming process (equations (10)-(12)) (Song and Pan, 2004) can potentially replace the cogeneration Scheme C. Tri-reforming of methane using CO<sub>2</sub> for the production of valuable syngas with desired ratio and reduction of carbon formation on catalyst was first implemented by Song and Pan (2004). The tri-reforming process fed with CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>O and O<sub>2</sub> with a molar ratio of 1: 0.475: 0.475: 0.1 is operated at 1 bar and 850°C (Song and Pan, 2004). The product gas contains H<sub>2</sub> to CO at a molar ratio of 1.68.



98% H<sub>2</sub> (1.5 kmol/s in this case) is separated from the product gas from gasification using pressure swing adsorption (PSA), which is then combined with the product gas from tri-reforming process. The remaining CO enriched gas from PSA is sent to gas turbine for electricity generation. A small amount of natural gas is needed to maintain an acceptable Wobbe Index for the gas turbine (Ng et al., 2010). Oxygen is used in an oxy-fuel gas turbine combustor, avoiding dilution of the fuel gas with nitrogen, and thereby reducing nitrogen in the downstream tri-reforming and methanol synthesis processes. A highly concentrated CO<sub>2</sub> stream is resulted from gas turbine combustion. The exhaust gas from gas turbine is then routed to the tri-reforming process. 95% of the unreacted offgas from methanol synthesis are recycled to enhance the production of methanol, while the rest is

purged. The proposed integrated scheme 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-Bio-oil polygeneration with CCS (Error! Reference source not found.(e))

Bio-oil derived from fast pyrolysis of poplar wood is used as a feedstock in polygeneration Scheme E (similar to Scheme A that uses coal). The bio-oil is modelled using acetic acid, acetol and guaiacol. The results of bio-oil gasification performance were validated elsewhere (Ng and Sadhukhan, 2011a, 2011b). The operating conditions of some of the process units in Scheme A are adjusted to tailor for the bio-oil system. These include the temperature and pressure of the gasifier set at 1112°C and 30 bar. This is to attain thermally neutral gasification reaction condition. The product gas from the gasification contains 31% H<sub>2</sub>, 25% H<sub>2</sub>O, 32% CO and 12% CO<sub>2</sub> by mole. Steam is not required in WGS due to high water content in the product gas attributed to the high moisture content in bio-oil. The gas cleaning process excluded cyclone and H<sub>2</sub>S removal units since bio-oil is free from contaminants. Pre-combustion CCS is used to capture 85% of CO<sub>2</sub> in order to attain a stoichiometric ratio  $(H_2 - CO_2) / (CO + CO_2) = 2.05$ , desired for high yield of methanol (Ng and Sadhukhan, 2011a).

### 3.2 Polygeneration Scheme Performance Trade-offs

The analyses of process schemes A-E in terms of thermodynamic efficiency and net plant-wide emission and *EP* are presented in Table 7 and Table 8, respectively.

**Table 7**

**Table 8**

A comparison between Schemes A and B (polygeneration with CCS and with reuse, respectively) demonstrates that increasing the total value of products does not necessarily enhance an overall systems performance. Numerous trade-offs need to be considered. The total LHV of the

products from Scheme B is 85% higher than that from Scheme A (on the basis of Scheme A product LHV), due to the additional production of methane from captured CO<sub>2</sub>. In spite of this, the energy efficiency of Scheme B is lower than that in Scheme A attributed to the hydrogen requirement in the Sabatier's reaction (equation (9)) (Table 7). Scheme B has higher CO<sub>2</sub> emission per unit product than Scheme A, 8.3 t CO<sub>2</sub>/GWh compared to 7.7 t CO<sub>2</sub>/GWh, respectively (Table 7). The on-site generation of hydrogen in Scheme B is not sufficient to meet the entire requirement and thus additional hydrogen is imported. This leads to 3.8 times higher operating cost for Scheme B compared to Scheme A, on the basis of a price of hydrogen of 1104 Euro/t (Stiegel and Ramezan, 2006). Compared to the operating cost, the product value due to methane production in Scheme B is only increased by 1.2 times from Scheme A. As a result, the *EP* of Scheme B is lower than that of Scheme A, 16.2 million Euro/y and 139.9 million Euro/y, respectively (Table 8). Scheme A would thus be more desirable in terms of energy and emission performance improvement. If the value of methane increases to 51.3 Euro/MWh, both schemes would be cost-competitive (on the basis of 139.9 million Euro/y).

The negative *EP* from Scheme C suggests that the value of electricity generated does not offset the cost of CCS (Table 8). A price of 81 Euro/MWh of electricity has been estimated in order to achieve an economically viable Scheme C (*EP* > 0). Modification of a cogeneration system Scheme C into a polygeneration system Scheme D is likely to improve systems performances. The CO<sub>2</sub> emission per unit product from Scheme D (17 t CO<sub>2</sub>/GWh) is lower than that from Scheme C (128 t CO<sub>2</sub>/GWh) (Table 7). The advantage of Scheme D is that a substantial amount of methanol is produced by the integration of the post-combustion flue gas and natural gas in the tri-reforming process, increasing the overall value of the products that can compensate for the increased operating cost. There is a prominent improvement in the *EP*, from -13.1 million Euro/y in Scheme C to 317.2 million Euro/y in Scheme D (Table 8). As also observed from the study of Adams and Barton (2011), diverting captured CO<sub>2</sub> into liquid product is energetically more efficient and economically

more favourable under the current policy context, though the CO<sub>2</sub> reuse schemes do not save the total emission across life cycle, because eventually the products are consumed.

Scheme E, bio-oil polygeneration into methanol, acetic acid, hydrogen and electricity, is less efficient compared to analogous Scheme A using coal. This is primarily due to the lower LHV of bio-oil of 18 MJ/kg than 28 MJ/kg of coal and higher moisture content, i.e. 30 wt% of bio-oil and 12 wt% of coal, respectively (Larson and Tingjin, 2003; Ng and Sadhukhan, 2011a). Due to the thermal neutrality of the bio-oil gasification process, no excess steam is available for power production. Scheme E results in higher methanol production (CO conversion of 82%) (Ng and Sadhukhan, 2011a) than that from Scheme A (75%), however the acetic acid production from Scheme E is only half of that from Scheme A. Considering carbon sequestration during biomass growth, 66 t CO<sub>2</sub>/GWh emission from Scheme E can be eliminated. The netback of bio-oil in Scheme E, that indicates the maximum buy-in price of bio-oil (81.6 million Euro/y or 8.1 Euro/GJ), is lower than the *EP* of Scheme A (139.9 million Euro/y) (Table 8). The bio-oil polygeneration system may still compete with the coal based schemes, if renewable products from bio-oil are given credits. The overall bio-oil based product value must at least be increased by 5.8 Euro/GJ, for cost-competitive performance against coal. Banding of price structure at various levels is introduced under the Renewables Obligation in the UK. This is to ensure that the technologies at a demonstration stage receive support and incentives for further exploitation at a larger scale (DECC, 2011). Our previous studies have also indicated mechanisms to create economic incentives for bio-oil based polygeneration systems (Ng and Sadhukhan, 2011a, 2011b; Sadhukhan and Ng, 2011).

### *3.3 Ranking of Polygeneration Schemes*

*Which design is superior? Capture and store, capture and reuse or reuse without capturing CO<sub>2</sub>?*

Figure 7 presents the comparison of performances amongst Schemes A-D with respect to thermodynamic efficiency, CO<sub>2</sub> emission level and economic potential. Based on the performance analyses of Schemes A-D (Figure 1) detailed in section 3.2, the following ranking in the order of preference for these schemes can be established.

Highest to lowest thermodynamic efficiency:  $D > A > B > C$

Lowest to highest emission:  $A < B < D < C$

Highest to lowest *EP* per unit output energy:  $A > D > B > C$

### **Figure 7**

The analyses suggest that modification of a cogeneration system into a polygeneration system is likely to improve the systems performances, whilst revamping a polygeneration system by adding more products does not necessarily relate to a significant improvement.

The CO<sub>2</sub> reuse cases, i.e. Schemes B and D represent the direct and indirect utilisation of CO<sub>2</sub>, respectively. Scheme D, wherein post-combustion CO<sub>2</sub> without capture is converted into methanol through syngas platform has a more flexible configuration compared to Scheme B (polygeneration with CO<sub>2</sub> capture and reuse). It provides flexibility in syngas conditioning for the generation of other products, e.g. Fischer-Tropsch liquid, dimethyl ether etc. Most of the CO<sub>2</sub> reuse processes require hydrogen. A CO<sub>2</sub> reuse system self-sufficient in cost-effective hydrogen supply (without requiring any import or without including expensive hydrogen production technique) is highly envisaged, shown in Scheme D. The plant-wide emissions from reuse Schemes B and D are lower than that from CCS Schemes A and C. However, from whole system life cycle perspectives, reuse schemes can only slow down CO<sub>2</sub> release to the atmosphere. In contrast, 96% and 76% of CO<sub>2</sub> from Schemes A and C (Table 7), respectively, are captured and stored underground, where the CO<sub>2</sub> life cycle can be prolonged. Considering all these aspects, Scheme A is regarded as the ‘winner’

attributed to its high efficiency, low CO<sub>2</sub> emission from a whole system life cycle perspective and high *EP* per unit output energy.

### *The impact of carbon tax*

Based on the emission analysis of Schemes A-D (**Error! Reference source not found.**) in Table 7, the order of sensitivity of *EP* to carbon tax can be established as follows (from the lowest to the highest slope in Figure 8(a)).

Lowest to highest sensitivity to carbon tax:  $A < B < D < C$

Scheme A is able to withstand higher carbon tax rate, due to its high *EP* and low CO<sub>2</sub> emission. The *EP* only reduces to 102 million Euro/y for as high a carbon tax as 1000 Euro/t. Although less sensitive to carbon tax, levying carbon tax poses a great impact on Scheme B in view of its low *EP* that reduces to zero for a carbon tax of 235 Euro/t. Scheme D is more sensitive to carbon taxation than Schemes A and B, due to its higher CO<sub>2</sub> emission rate at 52.1 t/h compared to 8.7 t/h and 4.7 t/h from Schemes B and A, respectively. The carbon tax rate should be as high as 468 Euro/t, in order for Scheme D (best performance in reuse cases) to compete against Scheme A (best performance in CCS cases). At this point, the *EP* vs. carbon tax lines for Schemes A and D intercept, providing an *EP* of 122 million Euro/y. Negative *EP* for Scheme D is incurred above 762 Euro/t of carbon tax. There is no direct economic competition due to carbon tax between reuse Schemes B and D, unless the tax rate is as high as 900 Euro/t. It is recognised that based on the consideration of both the sensitivity to carbon tax as well as *EP*, a scheme with low *EP* and with high environmental emission can be penalised by carbon tax (e.g. Scheme B). Broadly speaking,

schemes with low *EP* and low emission are more likely to be susceptible to carbon tax than schemes with high *EP* and high emission (e.g. Scheme D). Obviously, schemes with high *EP* and low emission are the best options (Scheme A).

The maximum limit on CO<sub>2</sub> emission for *EP* = 0 for various carbon tax rates is investigated, using Scheme D as the base case, in Figure 8(b). The maximum limit on the CO<sub>2</sub> emission decreases exponentially from 32 million t/y to 6 million t/y with increasing carbon tax rate from 10 Euro/t to 50 Euro/t. Thus higher carbon tax rate lowers the total CO<sub>2</sub> emission and the economics of a system. Nevertheless, higher carbon tax rate at 40-50 Euro/t has shown 25% difference in the maximum limit, and it is expected that the difference will eventually become insignificant beyond carbon tax rate of 50 Euro/t due to the flattening of the exponential function. This forms a bottleneck with no further possibility of CO<sub>2</sub> emission reduction, even when the carbon tax rate is increased and thus carbon taxation essentially receded into the background.

The capital intensive CCS is likely to be realisable in industrialised nations. Annex I countries (UNFCCC, 2011) with high energy consumption per capita, stringent emission target, carbon tax and trading uncertainties, may opt for CCS in polygeneration schemes, such as Scheme A, whilst the reuse polygeneration schemes can become technologies of choice for developing economy in the interim period.

### **Figure 8**

#### *Bioenergy with carbon capture and storage*

The integration of carbon capture and storage in the biomass based energy systems, known as bioenergy carbon capture and storage technology, has recently generated significant interest (IPCC, 2005; Rhodes and Keith, 2008; McGlashan et al., 2010). Such a technology is capable of producing useful product while achieving negative net atmospheric carbon emissions and hence

generating more carbon credits. However, the prospect of this technology is unforeseeable due to a number of reasons such as the potential of utilisation of biomass in large scale production of fuels, chemicals and power; lack of experience and analysis (IPCC, 2005). In this study, Scheme E presents such an example. This scheme uses bio-oil instead of biomass as the feedstock. It has been found that Scheme E is less compelling compared to Scheme A with respect to the efficiency and the economic performance (Table 7 and Table 8). This imposes a greater challenge on the potential of bio-oil in substituting fossil fuels. However, by comparing between a conventional coal IGCC system (Scheme C) and a bio-oil polygeneration system (Scheme E), the latter can be beneficial, provided that the cost of bio-oil can be reduced to a significant extent.

One may argue that CO<sub>2</sub> storage is not necessary since biomass is regarded as carbon neutral source, because the CO<sub>2</sub> emitted can be re-captured by plants and crops. This is true as long as the rate of absorption of CO<sub>2</sub> by biomass crops is almost equal to the rate of emission of CO<sub>2</sub>, and assuming that the amount of crops is more than sufficient to absorb the CO<sub>2</sub>. This could be difficult if biomass crops within a particular area are largely harvested for the utilisation in a large scale system, and the plantation of biomass crops is not rapid enough to cope with the emission of CO<sub>2</sub> from large scale polygeneration systems. IPCC pointed out that bioenergy with carbon capture and storage technology is realisable once the economies of scale are improved, via three possibilities (IPCC, 2005):

- Nearby CO<sub>2</sub> pipeline is available
- Co-processing of biomass with coal
- Scaling up the biomass energy plant for larger production

#### **4. Conclusions**

This paper presents performance evaluation of decarbonised polygeneration systems primarily exploiting gasification routes, in terms of energy efficiency, economic, CO<sub>2</sub> emission and economic sensitivity to carbon tax, through systematic techno-economic studies which embraced process simulation, energy integration and economic evaluation approaches. Various capital and energy intensive CO<sub>2</sub> emission minimisation processes such as CCS, capture and reuse producing methane using Sabatier's reaction as well as reuse without capture producing methanol using syngas tri-reforming based platform have been investigated for the techno-economic feasibility of integration into primarily power production facilities utilising coal, biomass / bio-oil feedstocks. With an aim of investigation whether increasing product portfolio, such as, hydrogen, acetic acid, methanol, methane etc. from a power plant or converting a cogeneration plant into a polygeneration plant by CO<sub>2</sub> reuse eliminating the need for CO<sub>2</sub> storage, makes any economic sense, the following conclusions are made.

Highest to lowest thermodynamic efficiency of the schemes:  $D > A > B > C$

Lowest to highest emission:  $A < B < D < C$

Highest to lowest *EP* per unit output energy:  $A > D > B > C$

Lowest to highest sensitivity to carbon tax:  $A < B < D < C$

Scheme A = Coal CCS producing electricity, hydrogen, acetic acid and methanol according to demands.

Scheme B = Production of electricity, hydrogen, acetic acid and methanol and methane from the captured carbon dioxide utilising coal

Scheme C = Coal integrated gasification combined cycle with CCS.

Scheme D = Production of electricity from combined cycle and methanol from natural gas tri-reforming utilising coal.

Scheme E, similar to Scheme A, processes bio-oil as an alternative low carbon feedstock. While bio-oil creates environmental incentives, its economic competitiveness is uncertain and can be

enhanced by introducing credits on product prices. Promising results in terms of improved energy efficiency from 36% in IGCC with CCS scheme to above 70% in polygeneration schemes, viable *EP* and a minimum of 75% of plant-wide CO<sub>2</sub> emission reduction demonstrate that the polygeneration Schemes A, D and E can become low carbon technologies of choice.

The present study has contributed some distinguished concepts on synthesising favourable energy production routes which can be realised in the near future. The design of these advanced technologies embraced several important aspects: high energy efficiency, economically compelling and environmentally benign. The consideration of incorporating CO<sub>2</sub> reuse pathway has been demonstrated to be a viable option, subject to the design and integration strategies as well as the nature of the parent system. Modification of an existing polygeneration system by including more products may not always create economic incentives, while the performance of a cogeneration system can be improved by converting it into a polygeneration system. The reuse of CO<sub>2</sub> can be beneficial depending upon the overall integration strategies as well as the nature of the CO<sub>2</sub> conversion process. The processes under consideration such as Sabatier's and reforming reaction processes, evolved from thermodynamic and process integration synergies, show higher thermodynamic efficiencies and economic potential compared to their counterpart based CCS schemes. The polygeneration schemes not dependent on external market for hydrogen supply or manufacturing player, show better economic incentives. Obviously, the CO<sub>2</sub> reuse pathways less effectively slow down CO<sub>2</sub> emission to atmosphere and are more sensitive to CO<sub>2</sub> taxation, compared to CCS.

Polygeneration system exploiting a low carbon feedstock (as exemplified using bio-oil) may still compete with the coal based polygeneration systems, if renewable products from bio-oil are given credits. Given that industrialisation will even be at a faster pace and that there will be an unmet need for fully integrated environmental and economic policies in the interim phase, flexible CO<sub>2</sub> reuse into fuel and chemical productions will be part of low carbon technology roadmap for

some countries in the interim period before the risks associated with CCS are more holistically addressed. For moving the low carbon technology forward, thus polygeneration by symbiotic CO<sub>2</sub> reuse strategies will be an efficient way.

### **Nomenclatures**

<i>CC</i>	Annual capital cost
<i>EP</i>	Economic potential
<i>H</i>	Total number of operating hours per year
$\Delta H_R^\circ$	Standard enthalpy change of reaction
<i>N</i>	Number of events derived from Counting Principle
<i>NP</i>	Total number of products
<i>OC</i>	Annual operating cost
$p_i$	Unit price of product <i>i</i>
$r_i$	Production rate of product <i>i</i>
$\theta$	Scale factor, equation (6)

### **Appendix A**

The economic parameters required for evaluating capital and operating costs are presented in Table A.1 and Table A.2, respectively.

#### **Table A.1**

#### **Table A.2**

### **Appendix B**

Additional data are provided for modelling systems in Schemes C, D and E in ASPEN Plus, summarised in Table B.1.

## Table B.1

### **Acknowledgement**

The authors express their gratitude to The University of Manchester Alumni Fund and Process Integration Research Consortium for financial aid to support this research.

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