1 Assessment of industrial by-product synergies from process

2 engineering and sustainability principles

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- 4 Feisal Ali Mohammed, Wahidul K. Biswas*, Hong Mei Yao and
- 5 Moses Oludayo Tadé
- 6 Faculty of Engineering
- 7 Curtin University, GPO Box U1987, Perth, WA 6845, Australia
- 8 Fax:+61-08-92664811
- 9 Email:feisal ali mohammed@yahoo.com
- 10 Email: w.biswas@curtin.edu.au
- 11 Email: H. Yao@exchange.curtin.edu.au
- 12 Email:M.O.Tade@curtin.edu.au
- *Corresponding author

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- 15 Abstract: Industrial synergy has long been one of the applications of industrial ecology; popularised in
- the 1980's. Industrial synergy increases the interaction between industries through the utilisation of
- wastes/by-products, thereby offering a closed-loop system. A target application for industrial synergy
- 18 is Primary industry which generates a huge amount of waste. Historically however, most existing
- 19 synergies have been unplanned and were established by interested industries. To date, new symbiotic
- 20 relations have not been considered in any depth due to a lack of systematic analysis and
- 21 implementation procedures. This research aims to bridge this gap by developing a framework for the
- 22 evaluation and implementation of new synergies, incorporating both process engineering concepts and
- 23 sustainability principles. The framework will use the Kwinana Industrial Area (KIA) of Western
- 24 Australia as a case study, whereby four by-products will be identified and pre-evaluated for their
- potential synergies. The sustainability benefits of these synergies will then be assessed from a social,
- 26 economic and environmental perspective.

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- 32 pp.?-?.
- 33 Biographical notes: Feisal Ali Mohammed is a PhD candidate at the Department of Chemical
- 34 Engineering, Curtin University. The title of his PhD research is 'A Framework for Synergy Evaluation

- 1 and Development in Heavy Industries'. He was graduated with a BSc degree in Chemical Engineering
- 2 Degree from Curtin University of Technology, Malaysia.
- 3 Dr Wahidul K. Biswas is a Senior Lecturer and Program Coordinator at the Sustainable Engineering
- 4 Group, Curtin University. He teaches a core engineering unit on Engineering for Sustainable
- 5 Development to all engineering students at Curtin University. Wahidul has carried out extensive life
- 6 cycle assessment research on environmental emissions from the Australian agricultural, alternative
- 7 fuels, building and construction, manufacturing, mining, gas and water sectors.
- 8 Dr Hong Mei Yao is a Research Fellow at the Department of Chemical Engineering, Curtin
- 9 University. Her specific expertise are in modelling, simulation, optimisation, and control design for
- 10 industrial complex system using frontier mathematical tools. Her research activities have covered a
- 11 range of applications including bioprocess, combustion process, wastewater treatment, industrial
- waste management, chromatographic separation, process integration and industrial ecology.
- 13 Professor Moses Tadé is the Dean of Engineering and holds the Personal Chair of Process Systems
- 14 Engineering at Curtin University, Perth, Western Australia. He is a John Curtin Distinguished
- Professor in recognition of his ongoing contributions to the University. He is the joint Director of the
- 16 Centre for Process Systems Computations (CPSC). His research includes: biochemical engineering;
- process modelling and simulation; process optimisation and control; process systems engineering.

19 1 Introduction

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- The main objective of resource-based industries is not only to minimise production costs in order to
- 22 maximise profits, but also to avoid environmental impact (Azapagic, 2004; Broadhurst and Petrie,
- 23 2010). In the era of climate-change, where ever-changing and stringent environmental regulations are
- 24 enacted, industries are required to rethink and redesign industrial processes from scratch. Hence, new
- 25 concepts, designs and processes from sustainable development, such as process intensification,
- 26 flexible and miniaturised plants, localised production, and industrial ecology have become
- 27 mainstream.

Industrial ecology (IE), is the study of material and energy flows between industrial systems, and their effects on the environment (Edward, 2004; Diwekar, 2005). Research into IE has grown rapidly but has been primarily focused on a particular industrial zone or targeted at the conceptual design of new plants and processes (Nikolopoulou et al., 2012). There have been several IE studies on existing industries and the linkage of their wastes/ by-products to industrial symbiosis (Kurup et. al. 2005; van Beers, 2009;Biswas and Cooling, 2013). However, these studies did not take into account lifecycle analysis when assessing the environmental implications of synergies, and they have primarily focused on the application of sustainability principles to existing synergies. In addition, most of the current industrial synergies in use are seldom developed from organic streams. In the methodology of environmental impact studies, a major tool used is the Life Cycle Assessment (LCA), which assesses the environmental impact of a product at each stage of its lifecycle (Diwekar, 2005). Despite this, the use of the LCA is restricted as it can only evaluate the environmental effects of a single process at any one time. To overcome this limitation, Gerber et al. (2011) developed a method whereby the LCA could accommodate various product uses and alternative processes. The idea of integrating process

synthesis with a LCA applied in IE (Diwekar and Shastri, 2010) has created opportunities for process engineers to work closely with environmental scientists.

The aim of the current research is to overcome the identified shortcomings by developing a framework that will incorporate both process engineering and sustainability principles to produce new and unexplored synergies. The involvement of "green" process engineering in synergy implementation will essentially convert by-products to useful resources, and thus aid in achieving a closed-loop system with zero discharge.

The paper begins with a generic outline of typical industrial symbiotic relations as a first step in identifying potential by-products before introducing the methodology of the proposed framework. It continues with the introduction of the Kwinana Industrial Area (KIA) which was used as a case study for the implementation of this framework. Subsequently, potential by-product synergies evaluated at KIA are presented, followed by the results of a preliminary sustainability assessment. Finally, the paper concludes with some recommendations.

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2 Framework for by-product assessment and new synergy establishment

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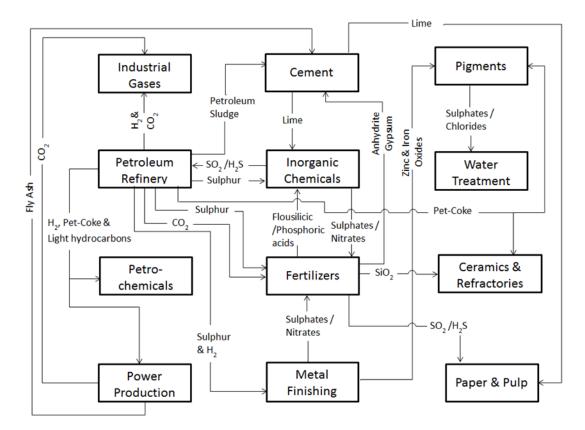
- 17 There is a plethora of chemicals and products manufactured globally, largely supplied by Primary and
- major mineral processing industries. To this effect, a generic symbiotic relation between these
- 19 industries is proposed as a first step in supporting the symbiosis evaluation in the proposed
- 20 framework.

2.1 Premises of the framework

- 22 The generic outlay in Figure 1(below) classifies industries into groups, based on manufacturing
- 23 processes and product properties. The industries on the left side are identified as major sources of
- wastes/ by-products. In the middle of the figure, there are the core industries which generate most of
- 25 the synergies. This is due to their ability to utilise the by-products of neighbouring industries as
- 25 the synergies. This is due to their ability to diffuse the by-products of neighbouring industries as
- 26 inputs, and their ability to provide by-products to other industries. The right side of the figure
- 27 represents the industries that can form synergies, mainly by utilising by-products from other
- 28 industries.

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Figure 1 Generic industrial symbiotic relationship



Depending on the solvents/reducing agents used; different by-products are generated. The three most commonly used reducing agents are nitric, sulphuric and hydrochloric acid. Thus, many of the by-products produced are in the form of nitrates, sulphates or chlorides. Using the generic framework above, one can firstly identify possible by-products from particular industries and also identify the recipient industries that have the potential to form synergies. The sustainability benefits of these by-product synergies can then be assessed and are discussed in the subsequent sections.

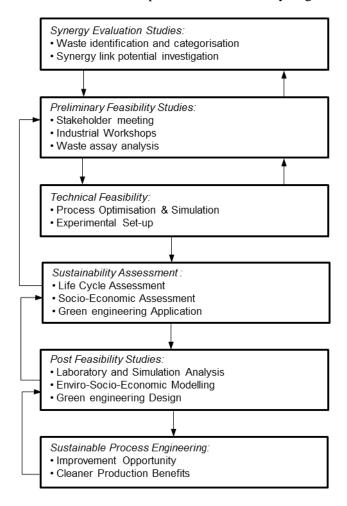
The purpose of this generic outline is to promote the implementation of industrial symbiosis from local to regional levels. Therefore, instead of focusing on a single industrial area, greater coordination between industries within a specific region is proposed. However, challenges will be presented in the form of geographical proximity, and infrastructural constraints and their costs such as pipelines between industries and market changes.

After the identification of potential by-products, the application of the framework will be carried out to investigate the practicability for synergy realisation.

2.2 The sustainability framework

 Figure 2 highlights the steps of the sustainability framework and shows the technical and sustainable aspects of synergy assessment.

1 Figure 2 Framework for the evaluation and implementation of new synergies



As can be seen above, potential by-products are firstly identified with the aid of the generic outlay. This is followed by an investigation into the available recipient industries that can form by-product synergies. After the establishment of synergy linkages, studies on their economic and environmental feasibility are assessed and then presented to relevant industries for feedback. Industrial workshops are then organised to justify the suitability and practicality of synergies.

From the framework, objectives for mutually agreed practicable synergies with industry were made and feed requirements for the recipient industry clarified. Thereafter, processing paths for effectively meeting the set objectives were assessed both theoretically via optimisation and simulation, and practically through laboratory experimentation with available industrial samples and data.

Sustainability and "green" engineering principles were further applied to the selection of the most suitable processing requirements for forming the symbiosis. This was complemented by a lifecycle analysis of environmental and economic objectives. Further necessary measures were taken via "green" engineering design to address any shortcomings regarding the environmental objectives. The results of the sustainability assessment were then presented to relevant industries for further feedback.

In the next stage, a pilot plant will be designed and implemented following a set process synthesis and sustainable parameters. Based on the results of the pilot plant, improvement opportunities could

be seen whereby more effective results could be obtained, or any issues solved that might arise prior
 to deeming industrial application as suitable.

The practical application of the framework to a case study is anticipated to take place in the near future and will be conducted on identified potential symbioses at Kwinana Industrial Area (KIA). This paper only presents the results from the by-product assessment and synergy pre-feasibility studies, which are elaborated upon in the subsequent sections.

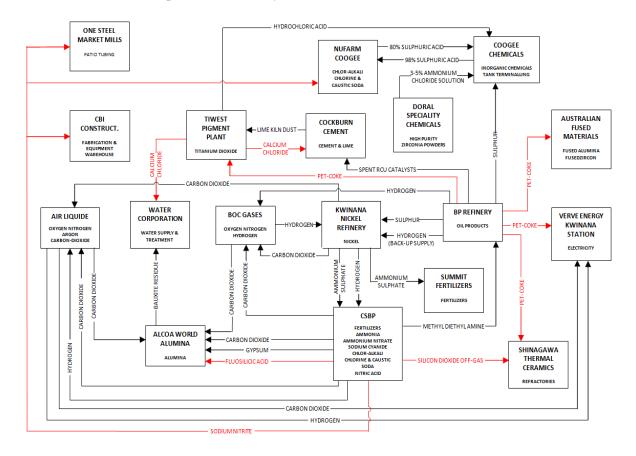
3 Case study at Kwinana Industrial Area (KIA)

KIA is by far the largest and most diverse industrial processing region (with supporting industries) in Western Australia. It consists of large inorganic mineral processing industries, chemical industries, an oil refinery, fertiliser manufacturer, and a number of other minor industries. This area is known for its many by-product synergies where materials and utilities are shared; wastes from one company are often inputs for another. However, as with elsewhere globally, KIA is facing sustainability challenges on various fronts, including water and energy scarcity, climate-change, an ageing workforce, and growing community sustainability expectations. Sustainability studies at KIA have suggested four areas that can be further focused upon (Van Beers, 2008). These are: the use of inorganic mineral wastes, enhancing by-product synergies, waste water utilisation and energy economy. The presence of various types of industries and their resultant by-product volumes within Kwinana are the main reason for choosing KIA as a case study.

3.1 By-product identification

- Through application of the framework at KIA, four by-products: petroleum coke, phosphate rock digestion off-gases, nitrogen oxides (NO₂) waste gases, and calcium chloride (CaCl₂), have been identified for their potential in the development of new relationship among industries. This identification has decided upon due to the amount of supply, the ease of post-processing or treatment, and the availability of candidate industries for symbiosis formations. The proposed synergies are presented in Figure 3 in red, with existing relations also depicted for reference.
 - As a result of preliminary synergy evaluation and pre-feasibility studies, it can be shown that with the application of industrial ecology, the by-products in question can be reused as feed materials by other industries.

1 Figure 3 Current and Proposed Industrial Symbiotic Relations at KIA



3.2 Preliminary sustainability assessment

A hypothetical example, based on the triple bottom-line perspective was applied to the identified synergies in Kwinana. Typical results are summarised in Table 1. The sustainability implication of each identified relationship is also summarised in the table.

3.2.1 Petroleum coke (pet-coke)

Pet-coke has potential synergetic use as a feed material in the production of titanium dioxide pigment and the production of Zircon or the manufacture of silicon carbide as a constituent of thermal ceramics. Further potential, based on the calorific value (energy output) of pet-coke, is in electricity generation to supplement coal-fired plants. These uses can provide economic incentives from the sale of pet-coke and higher energy outputs. Pet-coke's low volatile combustion matter and low ash content has social benefits in that health hazards to the surrounding population are reduced. The coke can also be mixed with low calorific coal to improve energy output, making the use of such coals more feasible (Predel, 2006). Although pet-coke is not used in large volumes at KIA, the reference to pet-coke synergy is used as an example to demonstrate the benefit of the by-product in areas where it is produced in large volumes.

1 Table 1 Sustainability Matrix of Identified Synergies

| By-product | Further use | Preliminary Sustainability Assessment | | |
|---------------------|-------------------------------|--|--|---|
| | | Social | Economic | Environmental |
| Calcium Chloride | Dust Suppressant | Respiratory effects from fine dust avoided | Easy to contain dust and avoid fines from dust emissions | Chemical release due to dust containment avoided |
| | Waste water treatment | Less competition for water use from industries | Less water use from other sources saving on costs and avoiding fines from waste water | Release of toxic chemicals to environment and ground water contamination avoided |
| | Cement additive | Improved structure life leading to less burdens from tax to fix them | Reduction of alkalis increasing cement/concrete life | Avoids CaCl ₂ release to marine environment |
| | SDOOL avoided disposal | Aesthetics and less effects from seafood derived from the SDOOL area | Fees from SDOOL disposal and monitoring costs avoided. Revenue from CaCl ₂ | Less chances of environmental effect by avoiding marine release |
| Petroleum Coke | Natural coke substitute | Not identified | Cheaper alternative | Less use of virgin resources |
| | Electricity generation | Less emissions meaning less health effects | Higher calorific value meaning less costs compared to other cokes | Lower CO ₂ and toxic emissions to other cokes leading to less environmental effects |
| Nitrogen Oxides | Sodium nitrate production | Less acidic rain and adverse effects of nitrogen oxides to health by avoiding release | Fines resulting from emissions avoided, making savings to company. Revenue from the sale of ammonium nitrate | Less environmental burdens by avoiding nitrogen oxide emissions. Avoid virgin resource use through substitution or blending of ammonium nitrate with sodium nitrate in safety explosives |
| Phosphate Rock | Silicon dioxide supply to AFM | Less effects by avoiding long-term exposure to SiO ₂ , minimising health risks | Revenue from SiO ₂ sales | Not identified |

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3 3.2.2 Phosphate rock digestion off-gases

- 4 There are economic potentials for the use of acid SiO₂ off-gas at KIA. Flousilicic acid (H₂SiF₆) could
- 5 be utilised as a resource to produce aluminium fluoride, which is useful for the production of
- 6 aluminium metal from alumina. The challenge would be to attract investment in such an industry and
- 7 incentives can be found in the availability of H₂SiF₆ acid and alumina in the vicinity. The SiO₂
- 8 produced could be sold as raw material to a Zircon manufacturer, supplementing the SiO_2 feed
- 9 required for its production. In utilising SiO₂ to form synergies, there is a reduced risk of contact from
- 10 the gas with the surrounding community. There is also a reduced risk to workers from long-term
- 11 exposure during the working life of a phosphate digestion plant.

3.2.3 Nitric acid production tail gases

- 2 A suitable strategy which could be employed by a nitric acid plant at KIA to control nitrogen oxide
- 3 emissions is the use of sodium hydroxide. It could be used in a series of counter current absorption
- 4 processes to produce either sodium nitrite (NaNO₂) or sodium nitrate (NaNO₃) and water. This would
- 5 effectively reduce its carbon footprint, but it can also form several synergies from the by-products
- 6 formed from the process.
 - Sodium nitrate can be used for: (a) the manufacture of safety explosives for the mining industry; (b) as an agricultural fertiliser; (c) the regeneration of spent sulphuric acid from chemical manufacturing; (d) as a refining agent for air bubble removal in the glass and enamel industries. Sodium nitrite has uses analogous to sodium nitrate; mixtures of both are utilised in many applications. Sodium nitrite can be used for the synthesis of pesticides, as a de-scaling agent (oxide removal) for steel and as an additive to concrete in the fabrication and construction industry. These synergies can then improve the balance-sheets of the nitric acid plant. In addition, there are social benefits brought about by reduced nitrogen oxide emissions. These include lower health risks associated with inhalation that could cause respiratory failure and skin or eye burns from exposure to gases in high concentrations. Acidic rain brought about by the presence of gases in the air will also be lowered, which would further lessen health and environmental risks.

- 3.2.4 Calcium chloride from titanium dioxide pigment plant
- The potential uses of CaCl₂ within Kwinana include:
- in water treatment as a flocculent for solid removal
 - as a dust suppressant, or for the removal of unwanted water due to its hygroscopic or deliquescent nature (ability to absorb moisture)
 - as a kiln additive during cement production where it controls and eliminates alkali content which causes unwanted expansive reactions in concrete.

One of the major challenges faced in Kwinana is the dust produced by several mineral processing industries, a cement manufacturer and a coal driven power station. CaCl₂ could be used to control and tackle this challenge. This would result in benefits to industrial operations and to the community around Kwinana. Environment conditions would also be improved with the eco-system being less exposed to various compounds contained in dust. The re-use of this by-product would also place a lesser burden on the marine environment where it is usually disposed of. For the company, there would be cost-savings on licensing and monitoring. CaCl₂ could also form synergies with the water-treatment and cement industries. This would have economic advantages for all companies involved in the synergies.

Based on the literature review undertaken, the existence of similar synergy implementations in practice has not been established. However, established technologies for capturing nitrogen oxide emissions from nitric acid plants, hydrosilicic acid and silicon dioxide off-gas from phosphate rock digestion are employed worldwide. The only remaining aspect is to establish synergy relations by determining the acceptable form of purity required by processes that may use them. Petroleum coke on the other hand, is a pure by-product and is used as a source of synthesised coke. It is actually sold as a product by refineries that produce it in bulk – mostly in North America and Europe. Synergetic relations are thus easier for implementation. The challenge however, would be with the synergy of the

calcium chloride in terms of processing it to an acceptable standard for re-use. Nevertheless, its potential is great and thus its evaluation for implementation is warranted in the developed framework.

4 Conclusions and recommendations

The Kwinana Industrial Area is a good example in practice where various bodies and industries have made a concerted effort to foster synergies and reduce wastes. In the aim of promoting further industrial synergies, a framework has been developed to assess by-products and establish potential synergy relations.

In the analysis of identified synergies, the use of flousilicic acid and pet-coke for aluminium fluoride and carbon disulphide productions respectively, involve entry of new industries that are currently non-existent in Kwinana. The synergies of pet-coke are easily implementable as pet-coke does not require purification or post-processing and can directly replace coal or coke. The synergies of silicon-dioxide (phosphate rock digestion) and calcium chloride may need pre-treatment prior to their use. Many industries using these materials in their raw state have pre-processing facilities for purification or water removal. Although there are some costs involved in their implementation, the benefits realised by the synergies far outweigh the associated costs involved. Instead of employing low nitrogen oxide burners or expensive catalytic reduction technologies, the nitrogen oxide waste gases synergy could add value to the nitric acid plant and increase economic viability while satisfying environmental requirements. Additionally, the raw material (NaOH solution) required to form a value added product (sodium nitrite/nitrate) can be sourced within KIA.

In conclusion, the opportunities for further synergies at KIA and other industries elsewhere are worth investigating. If they are fully captured and implemented, they may one day bridge the finite resources dilemma that faces these industries.

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