

P-graph Method for Optimal Synthesis of Philippine Agricultural Waste-based Integrated Biorefinery

Kim Patrick H. Sangalang^a, Beatriz A. Belmonte^a, Jey-R S. Ventura^b, Viknesh Andiappan^c, Michael Francis D. Benjamin^{a,*}

^aResearch Center for the Natural and Applied Sciences / Chemical Engineering Department, University of Santo Tomas, España Blvd., 1015 Manila, Philippines

^bDepartment of Engineering Science, College of Engineering and Agro-Industrial Technology, University of the Philippines \ Los Baños, College, Los Baños, Laguna, 4031, Philippines

^cSchool of Engineering and Physical Sciences, Heriot-Watt University Malaysia, 62200, Putrajaya, Wilayah Persekutuan Putrajaya, Malaysia
 mdbenjamin@ust.edu.ph

An integrated biorefinery (IBR) is a potential source of sustainable energy, biochemicals, and other high-value products. This biomass processing facility is developed by maximizing material and energy product (or by-product) exchanges between process units within an industrial plant. In the Philippines, vast amounts of agricultural residues (e.g., rice husk) remain to be tapped for bioenergy production. Aside from this, designing a viable and sustainable IBR is a challenging task due to the highly integrated nature of this system. In this work, a P-graph (process graph) based method is applied to generate optimal and near-optimal IBR configurations utilizing Philippine agricultural waste as feedstock whose objective is to maximize profitability. The P-graph framework was initially created to solve process network synthesis (PNS), but recently, researchers extended its use beyond the PNS domain (i.e., integrated systems). In addition, the P-graph software presents the results in a graphical interface, a distinct advantage compared to other optimization techniques. A case study utilizing waste from rice production in the Philippines is used to demonstrate the methodology. The resulting model shows the optimal configuration of the IBR and the maximum profit generated 1,208.17 USD/h. Local government units can use results from this work in creating policies to maximize bioenergy production and increase the revenue generation of farmers.

1. Introduction

Carbon pollution from the consumption of fossil fuels dramatically contributes to the current global climate crisis. Presently, eighty percent of the primary energy consumed in the world is derived from fossil fuels, and 58 % is from the demand of the transport sector (Raud et al., 2019). With the increasing demand and declining supply for fossil fuels globally, the use of alternative fuels that are both renewable and sustainable is imperative. One of the most promising renewable energy sources is bioenergy, which can be produced from the utilization of agricultural residues. As an agricultural country, the Philippines could use biomass from rice production as a source of renewable energy to reduce fossil fuel dependency (Go et al., 2019). Across Asia, rice plantations have increased continuously due to the high demand for rice, resulting in increased generation of available biomass resources. The biomass from producing rice includes its straw, husk, and bran, which are underutilized despite having a relatively high economic value (Darmawan et al., 2018). A sustainable integrated rice mill complex was proposed by Lim et al. (2014) that considered the utilization of these by-products. Besides, various studies have been conducted to show that bioenergy and biochemicals can be sustainably produced from rice residues.

At present, sizeable agricultural waste generated in the Philippines remains untapped. In 2018, 19 Mt of rice had been produced in the Philippines based on the 2019 Selected Statistics on Agriculture (Mapa and Bautista, 2019). There is limited data available to account the agricultural waste generated by Philippine rice production.

However, existing literature can provide size ratios of rice residues with respect to the actual grain produced. According to the study of Peanparkdee and Iwamoto (2019), 1 kg of rice grain generates 1-1.5 kg of straw, 0.2 kg of husk, and 0.1 kg of bran. Several studies have proposed various process routes in utilizing rice residues for biorefinery operations. These include electricity generation through combustion of straw and husk (Aberilla et al., 2019), bioethanol production by lignocellulosic fermentation of straw (Tewfik et al., 2015), biodiesel production through transesterification of bran oil (Nguyen et al., 2018), and biofertilizer production via anaerobic digestion of husk and livestock manure (Unrean et al., 2018). However, these routes may not be efficient when operated as stand-alone processes. If these process routes were integrated within the same facility, they would improve waste utilization, increase farmer income, and reduce environmental pollution. An Integrated Biorefinery (IBR) refers to this interconnected biomass processing facility that produces multiple bioenergy products such as bioethanol, biodiesel, biofertilizer, and electricity using feedstock, such as rice straw, rice husk, rice bran, and livestock manure. In general, IBRs decrease carbon emissions by avoiding the burning of agricultural waste, reducing fossil fuel dependence, decreased need for raw material inputs, and producing low-carbon fuels (Ubando et al., 2020). Designing IBRs are considered state-of-the-art and a potential alternative for sustainable production of bioenergy and fossil fuel replacement. It is essential to determine the appropriate method to design sustainable IBRs.

Process Network Synthesis (PNS) is a crucial aspect of developing a model for an IBR. Designing an IBR involves the identification of the objective and constraint functions. The objective function is usually expressed in terms of profitability, while the constraint functions include material balances of flow streams, operating costs, and capacity ranges of the process units. Once these parameters are identified, traditional mathematical programming methods such as Mixed Integer Linear Programming (MILP) as applied in the case of an integrated palm oil based-complex (Tan et al., 2020) and sago plantation design (Rajakal et al., 2020) and Mixed-Integer Nonlinear Programming (MINLP) can be used. These methods can determine optimal solutions, such as the optimal capacity of process units and the profit earned from the process network (Grossmann and Santibañez, 1980). However, these conventional approaches have several disadvantages for complex problems, because computations become challenging to perform due to the combinatorial nature of large process networks and the inability to show near-optimal solutions.

To address this problem, the P-graph (process graph), a graph-theoretic and combinatorial approach can be used. This can be employed in process synthesis to generate the superstructure of the system automatically, and it can provide both optimal solutions and n -best suboptimal solutions (Aviso et al., 2019). Operating units, materials, and flow streams can be illustrated using distinct symbols in P-graph software. Properties of the system, such as cost functions, capacities of process units, raw material supply, product demand, flow streams, and name of materials and process units, can also be specified. The results can then be displayed in a graphical interface, making it an efficient tool for immediate industrial applications.

Recent works on the use of P-graph method include risk analysis of various scales of integrated bioenergy systems based on criticality (Benjamin et al., 2017), optimal synthesis of large-scale carbon sequestration networks via addition of biochar in soils (Aviso et al., 2019), process design and optimization in achieving cleaner production (Fan et al., 2020a), incorporated in an induction approach to determine an expert's judgment in ranking negative emission technologies (Low et al., 2020), and as a decision support tool in developing an integrated design for a waste management system considering a circular economy approach (Fan et al., 2020b). Designing an optimized rice-based IBR based on P-graph utilizing local agricultural waste is a novel work in the context of the Philippine setting. This is the first work that employs P-graph method for the optimal synthesis of an IBR utilizing residues from rice production processes and facilities. This work can be used in designing IBR using available agricultural waste derived from a particular locality in the Philippines. This work is also relevant in all countries where rice is a staple crop. Various processes are incorporated into the design in order to produce several biofuels and biochemicals from rice residues sustainably. Also, optimal and sub-optimal solutions are presented in alternative designs of the rice-based IBR. The next sections are as follows: Problem statement and the P-graph Methodology are discussed. An IBR using waste from rice production is used as a Case Study, and the corresponding Results and Discussion are presented. Lastly, Conclusions and Future works are placed toward the end of the paper.

2. Problem statement

The formal problem statement is stated as follows. The rice-based IBR has n number of biomass-processing units, and each will be producing a unique bioenergy product stream, m . The input-output in each process unit is based on realistic material and energy balance taken from existing literature and is assumed to be scale-invariant. The network topology or connections between process units within the plant and product demands are also known. The unit price of each stream is given, as well as the cost function values for each unit. The objective is to optimally synthesize the IBR considering maximum annual profit for the plant.

3. P-Graph methodology

The P-graph methodology and software are based on graph theory and combinatorial algorithms to solve PNS (Friedler et al., 1992). It is a bipartite graph that represents a process system structure. A P-graph model is similar to an MILP model, but it is presented in graphical form, and the results may display more than one feasible solution (i.e., optimal and near-optimal) based on the given objective function. The graphical interface includes two kinds of vertices, and these are the M-type and the O-type vertices. The M-type vertex, denoted by a dot, corresponds to material and energy streams in the system, such as raw materials (e.g., rice residues), intermediates, and products (e.g., biofuels). On the other hand, the O-type vertex, denoted by a horizontal bar, represents the operating units (e.g., unit processes) in the network. The two vertices are linked by edges that denote stream flowrates. There are built-in axioms (i.e., five) that govern the P-graph method to differentiate the vertices and generate the solution structures. The approach is based on three core algorithms; these are maximal structure generator (MSG), solution structure generator (SSG), and the efficient advanced branch-and-bound (ABB) algorithm. The MSG is responsible for developing the entire structure of the system considering all the possible connections towards producing the end product. On the other hand, the SSG creates all feasible subsets of the MSG, and the ABB selects the best solution among the feasible subsets generated. P-graph Studio has integrated its two previous software (i.e., PNS Draw and PNS Studio) into one for designing process networks (P-graph, 2020). The recent version can now be used to design the PNS, create the links between processes, put stream flowrates, enter measurement units, operating capacity, cost of operating units, and price of materials in one interface. The feasible solution(s) will then be generated and displayed using the graphical version of the solution(s) in just one software. In this work, the integrated biorefinery design will be based on the supply of rice residues to estimate the production of biofuels and biochemicals resulting from the integrated processes.

4. Case study: rice-based integrated biorefinery

P-graph approach is used to design and optimize the rice-based IBR system. In this work, the process units are assumed to be scale-invariant and are represented as black boxes with fixed yield (or efficiency). The process data (i.e., ratios for the material and energy) for the IBR design are taken from various sources. In this work, rice straw and husk are fed into a boiler to supply electricity for three production lines. In the first production line, rice husk and livestock manure undergo anaerobic digestion using methanogenic bacteria to produce biofertilizer. For the second line, rice straw is broken down to fermentable sugars, which is further converted by microorganisms to bioethanol. For the third line, rice bran undergoes milling (Van Zeist et al., 2012) then transesterification using alkali catalysts to produce biodiesel.

Table 1 shows the IBR input-output ratios, in which the columns are regarded as a process vector with a fixed set of ratios for each process unit's material and energy balance. To illustrate, in the case of fermentation, 1 kg/h of rice straw and 0.093 kW of electricity is required to produce 0.1687 L/h of bioethanol. The negative sign indicates that a stream is an input to the process while the positive sign denotes that a stream is a product (output) generated. The normalized process data, using Table 1, relative to the main product, is illustrated in Figure 1 as a P-graph model. Aside from the process data, economic data are also gathered in order to account for the costs and profitability of the optimized process design.

Table 1: Input-Output Model for the Integrated Biorefinery

Materials	Anaerobic Digestion (Unrean et al., 2018)	Fermentation (Tewfik et al., 2015)	Transesterification (Nguyen et al., 2019; Van Zeist et al., 2012)	Combustion (Aberilla et al., 2019)
Biofertilizer (kg/h)	0.233	0	0	0
Bioethanol (L/h)	0	0.1687	0	0
Biodiesel (L/h)	0	0	0.1913	0
Energy for the Processes (kW)	- 1.5572	- 0.093	- 0.00411	2
Rice Husk (kg/h)	- 0.130	0	0	- 1.824
Livestock Manure (kg/h)	- 0.187	0	0	0
Rice Straw (kg/h)	0	- 1	0	- 1.875
Rice Bran (kg/h)	0	0	- 1	0

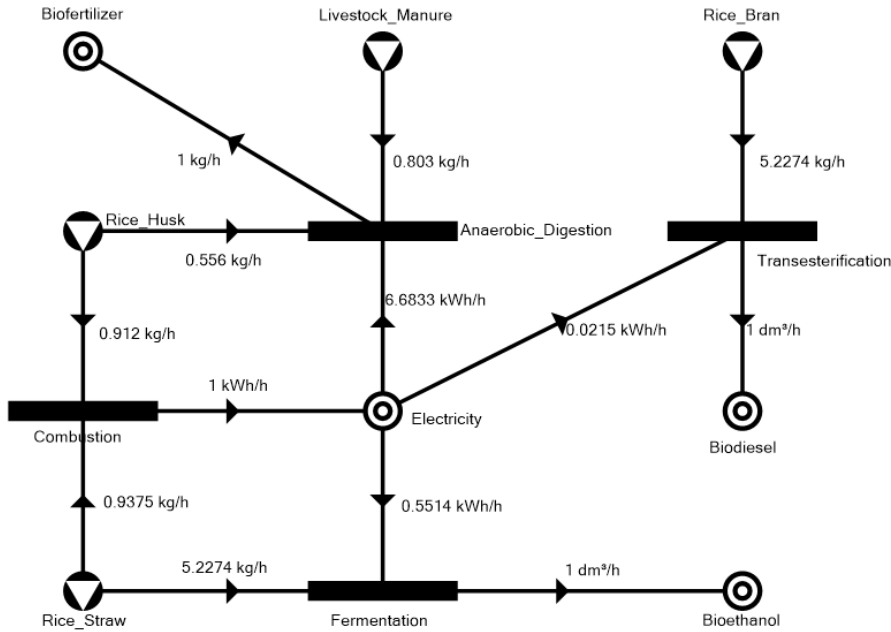


Figure 1: P-graph model of the rice-based IBR Case Study

The process data are based on the actual supply in one of the municipalities in Isabela, Philippines. The total rice farming hectare is based on 2,300 hectares, equivalent to an annual production of 15,732,000 kg of rice. 1 kg of rice grain generates an average of 1.25 kg of straw, 0.2 kg of husk, and 0.1 kg of bran (Peanparkdee and Iwamoto, 2019). Using these ratios, the rice residue generation can be calculated using the annual rice production estimate. On the other hand, the unit prices are based on the average retail prices of rice residues in Southeast Asia. The price and corresponding supply are as follows: For livestock manure = 0.014 USD/kg (5.00 kg/h), rice straw = 0.004 USD/kg (2,809.29 - 5,618.57 kg/h), rice husk = 0.09 USD/kg (449.49 - 898.97 kg/h), and rice bran = 0.12 USD/kg (224.74 - 449.49 kg/h).

The unit prices and product demand of biofertilizer (17.76 USD/kg, 7.14 - 142.86 kg/h), bioethanol (1.18 USD/L, 2,571.43 - 18,857.14 L/h), and biodiesel (0.84 USD/L, 4,457.14 - 25,714.29 L/h) are gathered from annual production reports and field interviews with the Philippine Department of Energy (DOE) and Department of Agriculture (DA). On the other hand, economic data for electricity (0.19 USD/kWh, 1,500 - 12,000 kW) are collected from the Philippine Power Situation Report (Capongcol et al., 2016). The fixed and variable costs of the process units (as shown in Table 2) are obtained by applying the costing methods for the biorefinery design of Tewfik et al. (2015) and Zhao et al. (2015). Using the mentioned process and economic data, these are encoded in the P-graph software. The feasible system structures, profit and cost per material, total profit, operating costs, and expected flowrates are then calculated.

Table 2: Cost Functions of Process Units

Process Unit	Cost Function Values	
	Fixed Cost	Variable Cost
Digester	72,885.93 USD	2.19 USD/kg Biofertilizer
Fermenter	43,731.56 USD	0.004 USD/L Bioethanol
Reactor	44,314.65 USD	0.002 USD/L Biodiesel
Boiler	55,393.31 USD	0.008 USD/kWh Electricity

5. Results and discussions

P-graph generated four feasible solutions for the case study, as presented in Table 3. The first or optimal solution involved the use of all operating units as shown in Figure 2. In Table 3, the second and third solutions eliminated transesterification and anaerobic digestion. The fourth solution excluded both transesterification and anaerobic digestion. Near-optimal solutions are deemed necessary when other factors not accounted for in the original problem statement are to be considered (i.e., the practicality of implementing the actual design). It can be seen from the table that all solutions are feasible. Based on the results, the IBR will operate at a profitable level, and

the optimal solution can potentially generate earnings of 1,208.17 USD/h. Despite having slightly lower profits, sub-optimal solutions can be implemented to allow flexible operation under various conditions. Solution 2 can be implemented if there is a low demand for biodiesel in the fuel market (e.g., excess local biodiesel supply). Solution 3 is recommended if there is a limited supply of livestock manure to be used in anaerobic digestion. Solution 4, on the other hand, focuses more on increasing the bioethanol production (i.e., 978.11 L/h).

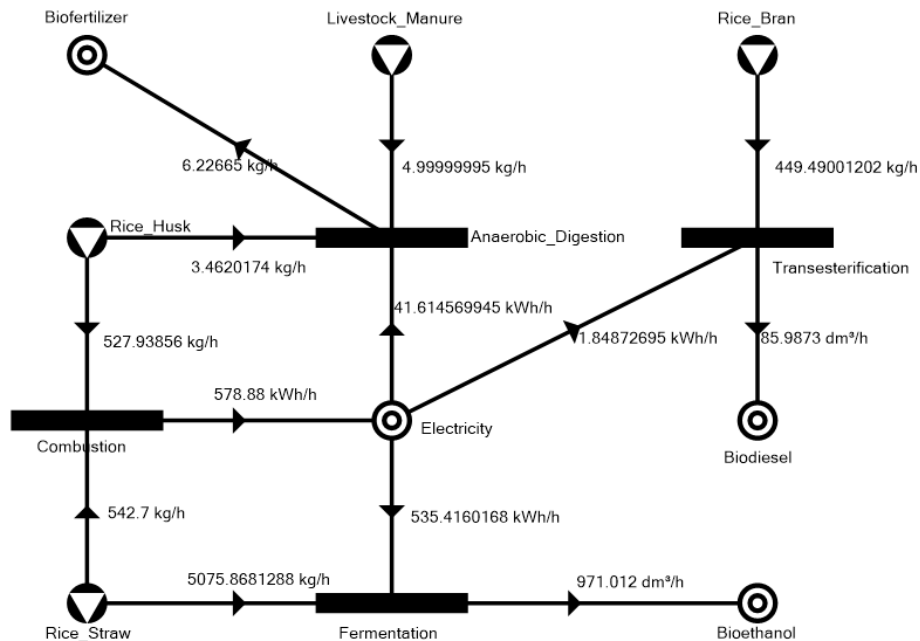


Figure 2: Optimal solution structure of the rice-based IBR Case Study

Table 3: Solutions Generated for the Case Study

Rank	Total Hourly Profit (USD/h)	Capacity of Process Units			
		Fermentation (L/h)	Transesterification (L/h)	Anaerobic Digestion (kg/h)	Combustion (kW)
Optimum	1,208.17	971.01	85.99	6.23	578.88
2 nd	1,192.72	971.31	-	6.23	577.20
3 rd	1,112.86	977.80	85.99	-	541.01
4 th	1,095.44	978.11	-	-	539.33

6. Conclusion and future works

A P-graph based methodology for the design of an integrated biorefinery was developed in this work using residues generated in the production of rice in the Philippines. The P-graph method was demonstrated using a case study on the utilization of rice residues through an integrated system that incorporates process routes for biofuel, biopower, and biochemical production. The use of P-graph in the design of the optimized model allows simple tracking of changes in the operating capacities and profit with variations in either the biomass supply or in the bioenergy product demands. This work can be used in the actual implementation of integrated biorefineries in a particular municipality in the Philippines and in other countries with abundant biomass sources. Future work will focus on extending this P-graph-based method to utilize other existing agricultural waste such as production residues of coconut, corn, and sugarcane.

Acknowledgment

Funding from the University of Santo Tomas through the Research Center for the Natural and Applied Sciences (UST-RCNAS) and the National Research Council of the Philippines (NRCP) Project No. G69 is gratefully acknowledged.

References

- Aberilla, J.M., Gallego-Schmid, A., Azapagic, A., 2019, Environmental sustainability of small-scale biomass power technologies for agricultural communities in developing countries, *Renewable Energy*, 141, 493–506.
- Aviso, K.B., Belmonte, B.A., Benjamin, M.F.D., Arogo, J.I.A., Coronel, A.L.O., Janairo, C.M.J., Tan, R.R., 2019, Synthesis of optimal and near-optimal biochar-based Carbon Management Networks with P-graph, *Journal of Cleaner Production*, 214, 893–901.
- Benjamin, M.F.D., Cayamanda, C.D., Tan, R.R., Razon, L.F., 2017, P-graph approach to criticality analysis in integrated bioenergy systems, *Clean Technologies and Environmental Policy*, 19(7), 1841–1854.
- Capongcol, M., Exconde, I., Ejercito, T., 2016, *Philippine Power Situation Report 2016*, Department of Energy - Electric Power Industry Management Bureau. 23-31.
- Darmawan, A., Fitrianto, A.C., Aziz, M., Tokimatsu, K., 2018, Integrated system of rice production and electricity generation, *Applied Energy*, 220, 672–680.
- Fan, Y.V., Chin, H.H., Klemeš, J.J., Varbanov, P.S., Liu, X., 2020a, Optimisation and process design tools for cleaner production, *Journal of Cleaner Production*, 247, 119181.
- Fan, Y.V., Klemeš, J.J., Walmsley, T.G., Bertók, B., 2020b, Implementing Circular Economy in municipal solid waste treatment system using P-graph, *Science of The Total Environment*, 701, 134652.
- Friedler, F., Tarjan, K., Huang, Y.W., Fan, L.T., 1992, Graph-theoretic approach to process synthesis: axioms and theorems, *Chemical Engineering Science*, 47(8), 1973-1988.
- Go, A.W., Conag, A.T., Igdon, R.M.B., Toledo, A.S., Malila, J. S., 2019, Potentials of agricultural and agro-industrial crop residues for the displacement of fossil fuels: A Philippine context. *Energy Strategy Reviews*, 23, 100–113.
- Grossmann, I.E., Santibañez, J., 1980, Applications of mixed-integer linear programming in process synthesis, *Computers and Chemical Engineering*, 4, 205-214.
- Lim, J.S., Manan, Z.A., Hashim, H., Wan Alwi, S.R., 2014, Synthesis of a sustainable integrated rice mill complex, *Journal of Cleaner Production*, 71, 118-127.
- Low, C., Ng, W., Putra, Z., Aviso, K., Promentilla, M., Tan, R.R., 2020, Induction approach via P-Graph to rank clean technologies, *Heliyon*, 6(1), e03083.
- Mapa, C. S., Bautista, R. P., 2019, Selected Statistics on Agriculture. Philippine Statistic Authority. 8-11. ISSN-2012-0352.
- Nguyen, D.D., Dharmaraja, J., Shobana, S., Sundaram, A., Chang, S.W., Kumar, G., Saratale, G. D., 2019, Transesterification and fuel characterization of rice bran oil: A biorefinery path, *Fuel*, 253, 975–987.
- Peanparkdee, M., Iwamoto, S., 2019, Bioactive compounds from by-products of rice cultivation and rice processing: Extraction and application in the food and pharmaceutical industries, *Trends in Food Science & Technology*, 86, 109–117.
- P-graph, 2020, P-graph Studio <www.p-graph.com> accessed 18.05.2020.
- Raud, M., Kikas, T., Sippula, O., Shurpali, N., 2019, Potentials and challenges in lignocellulosic biofuel production technology, *Renewable and Sustainable Energy Reviews*, 111, 44–56.
- Rajakal J.P., Ng D.K.S., Tan R.R., Andiappan V., Wan Y.K., 2020, Mathematical Optimisation Model for Management of Sago Palm Plantation Expansions, *Chemical Engineering Transactions*, 78, 109-114.
- Tan Y.D., Lim J.S., Wan Alwi S.R., 2020, Optimal design of integrated palm oil complex with palm oil mill effluent elimination strategy, *Chemical Engineering Transactions*, 78, 1-6.
- Tewfik, S.R., Abulnour, A.G.M., Sorour, M.H., 2015, Techno-economic and environmental aspects of the production of medium scale ligno-cellulosic ethanol under Egyptian conditions, *Egyptian Journal of Petroleum*, 24(4), 375–381.
- Ubando, A.T., Felix, C.B., Chen, W-H., 2020, Biorefineries in circular bioeconomy: A comprehensive review, *Bioresource Technology*, 299, 122585.
- Unrean, P., Fui, B.C.L., Rianawati, E., Acda, M., 2018, Comparative techno-economic assessment and environmental impacts of rice husk-to-fuel conversion technologies, *Energy*, 151, 581–593.
- Van Zeist, Z., Marinussen, M., Broekama, R., Groen, E., Kool, A., Dolman, M., Blonk, H., 2012, LCI data for the calculation tool Feedprint for greenhouse gas emissions of feed production and utilization. Dry Milling Industry - Blonk Consultants.
- Zhao, L., Zhang, X., Xu, J., Ou, X., Chang, S., Wu, M., 2015, Techno-economic analysis of bioethanol production from lignocellulosic biomass in China: Dilute-acid pretreatment and enzymatic hydrolysis of corn stover, *Energies*, 8(5), 4096–4117.