Green Chemistry principle: Ionic Liquids as a material teaching for vocational students

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Abstract. The development of human civilization is characterized by the type of material used by society. The rapid development of material engineering and technology produces a variety of advanced materials such as smart materials, natural materials, chemical materials, nanomaterials, and environmentally friendly materials. Ionic Liquids (ILs) have criteria that are expected to be environmentally friendly because of their Green Chemistry (GC). The vocational syllabus needs to be reconstructed to be able to adapt this material technological progress. The purpose of this study was to determine the opinions of lecturers on the adoption of Ionic Liquid material teaching materials in vocational education in an effort to deal with the use of environmentally friendly materials that are indispensable in the industrial field. The subject of the study was taken through a purposive sampling method. There were 5 lecturers in one of the private polytechnics. Data collection through questionnaires is intended to determine the views of lecturers on ionic fluid material teaching materials and analyze the material requirements to be adopted into the vocational curriculum. The investigation results show that the interest and willingness of the lecturer to study and disseminate reached a score of 80%, this means that the lecturer needed the Ionic Liquid material. However, the teacher's understanding score still needs to be improved, so that it is necessary to design an Ionic Liquid teaching material that is interesting and easy to understand by both lecturers and students. The implications of this study can be used as recommendations in learning to be able to enrich the syllabus by adding Ionic Liquid material teaching material as an indispensable teaching material along with technological advances in industry 4.0.

1. Introduction
The results of the direct survey analysis on the content of vocational teaching materials in one of the private polytechnics proved that teaching materials still contained old content with constant material in recent years. While the rapid development of science and technology changes are evidenced by the discovery of several advanced materials such as smart materials, natural materials, chemical materials, chemical materials, nano materials, advanced materials, and environmentally friendly materials such as "Ionic Liquids (ILs)" [1]. Green, because the material is non-flammable, vapor pressure is close to zero, a wide temperature range that allows the use of ionic liquids at low temperatures or room temperatures in the liquid phase. Its non-volatile and non-flammable nature allows this Ionic Liquid to be used as a reliable solvent replacing volatile and flammable organic solvents which have been used in the synthesis of chemical compounds. Flammability and volatility of organic solvents can cause disturbances in the natural balance, and can cause exposure to toxicity to users [2]. This is very contrary to the 12 principles
of Green Chemistry which suggest not to use ingredients that are toxic and can damage the surrounding environment [3]. There is a gap between the progress of this technology and the content of the teaching materials of the existing vocational curriculum. Syllabus / chemical engineering curriculum must be reconstructed to be able to insert Ionic Liquid material so that it can be a reference for vocational students to be able to have the competency to choose safe and environmentally friendly solvents, because this competency is very much needed in the planning and processing of chemicals as a standard chemical engineering specialist implied in the vocational curriculum in Indonesia. This competency is very important to convey in the vocational curriculum so that efforts are needed to be able to socialize the material to students and lecturers through teaching materials. The long term angle of Ionic Liquid material is discussed in the fields of science and technology, which was initiated from the discovery of the first Ionic Liquid in 1914 [4], but in the field of education and teaching it still requires considerable time to be able to socialize it.

Therefore Ionic Liquid teaching materials will be created with the orientation of Green Chemistry specifically for vocational students, but beforehand there will be an analysis of the needs of first Ionic Liquid teaching materials for five respondents of vocational lecturers (polytechnic).

2. Material and methods

2.1. Ionic Liquids

Ionic Liquid teaching materials need to be inserted into vocational curriculum / syllabus with the aim of enriching the knowledge of students and lecturers in the selection of Green Chemistry. Ionic liquids are a high-tech material that has some extraordinary characteristics, which make it more preferred than traditional types of solvents that have ever existed before. This is because (1) there is a solvating ability: ionic liquids are used as solvents, there are only ions, the reaction takes place in very different conditions compared to using water or ordinary organic solvents which are neutral molecules; (2) no / little vapour pressure: Ionic Liquid vapour pressure can be neglected which makes it important to minimize exposure to toxic volatile vapours such as in the case of organic solvents; (3) non-flammable; (4) high thermal, chemical and electrochemical stability; (5) large fluid range: wide temperature range between liquid and gas; (6) easy to recycle; (7) are very polar; (8) not coordinated; (9) incompatibility with water and other organic solvents; (10) chiral ionic liquids can control stereo selectivity; (11) which has a safer period (not decomposed); (12) has conductivity. Ionic liquids are materials that are only formed from anions and cations while solvents such as benzene, chloroform, methanol, water and others consist of neutral species [5].

Ionic liquids are very different from ionic salts [6]. Ionic salts are solid at room temperature. Ionic salt is an ionic compound formed because of the electrostatic forces between cations which are generally metals with non-metallic anions. In general, ionic materials can be liquid if heated at high temperatures, such as NaCl melts at a temperature of around 800°C, this makes the conditions very impractical especially when organic synthesis. Ionic liquids are a class of liquid salts with a melting point below 100 °C, even below room temperature. Ionic liquids formed from large and asymmetric organic cations as shown in Figure 1, are derivatives of imidazolium, pyridinium, pyrrolidinium, ammonium, phosphonium and sulfonium. Common anions include; halides, tetrachloroaluminate, hexafluorophosphate, tetrafluoroborate and bis (trifluoromethylsulfonyl) imides - which are inorganic and organic anions such as alkylsulfate, alkylsulfonate, p-toluenesulfonate (tosylate) and trifluoroacetate.
The properties of ionic liquids depend on the cations and their constituent anions. This provides great potential in designing Ionic Liquids for certain purposes [8]. Table 1 shows the types of Ionic Liquids.

### Table 1. Types of Ionic Liquids with physical-chemical properties (BASF).

| Type of Cation | Ionic Liquids | Melting point (°C) | Viskosity (mPa) | Densitas (gr/cm³) | Flash point (°C) | Solubility in Water |
|----------------|---------------|--------------------|----------------|------------------|-----------------|---------------------|
| Imidazolium     | 1-Ethyl-3-methylimidazolium tetrachloroaluminate (EMIM AlCl₄) | 9 | 26 | 1.3040 | 218 | react with water |
|                 | 1-Butyl-3-methylimidazolium tetrachloroaluminate (BMIM AlCl₄) | -10 | 32 | 1.2340 | 198.5 | react with water |
|                 | 1-Ethyl-3-methylimidazolium Hydrogen sulphate (BMIM HSO₄) | 28 | 4320 | 1.2770 | >249 | |
|                 | 1-Ethyl-3-methylimidazolium acetate (EMIM Asetat) | -10 | 93 | 1.0270 | 164 | infinity |
|                 | 1-ethyl-3-methylimidazolium thiocyanate (EMIMSCN) | < -20 | 22 | 1.1140 | 162 | infinity |
| Tetraalkil ammonium | Methyl-tri-n-butylammonium methylsulfate (MTBS) | 62 | | 179.5 | Infinity | |

The advantages of ionic liquids are; non-volatile, stable to heat up to 300°C, soluble in various organic-inorganic and organometallic compounds, properties such as polarity, hydrophilic or lipophilic can be adjusted and some physical and chemical properties. Ionic liquids are also classified as salts which have a melting point <100°C [9].
Based on the melting point data in Table 1, it is known that there is room temperature Ionic Liquid (RTIL) [10]. RTIL is a type of Ionic Liquid that is the focus of development because it is liquid at room temperature. The type of cation determines the density, viscosity, and lipophilic or hydrophilic properties of an ionic liquid. The longer the alkyl chain, the higher the viscosity. The hydrophobic / lipophilic nature of ionic liquids also increases with the length of the alkyl chain [11]. Meanwhile, the type of anion determines the acidic, basic or neutral nature of an ionic liquid. Anions such as Cl-, AlCl4-, HSO4-, BF4-, PF6- produce acidic ionic liquids while anions such as acetate provide alkaline properties [12].

Providing solvation media for chemical reactions and creating environmentally friendly reaction processes is the latest effort to replace the old provocative. For conduction of chemical processes and synthesis of materials, the aqueous and organic reaction media are always used. The availability of water as a solvent is very easy and inexpensive, non-flammable, non-toxic, and environmentally friendly [13]. However, the high or low temperature conditions of the reactions associated with organic solutes with water as solvents are a challenge to the temperature of the liquid range (0-100°C) and the limitations in dissolving each ingredient. Some organic solvents are explosive, flammable and toxic while ionic liquids are green solvents [14].

To improve work competence in the field of chemical engineering in the planning, preparation and processing of chemicals for production, it is necessary to add new knowledge about ionic liquids as green materials that can be a reference in the selection of environmentally friendly chemicals.

2.2. Green Chemistry (GC)
The rapid growth of the chemical industry has caused environmental problems. The loss of biological species in forests and in the waters, ozone depletion, agricultural pollution, freshwater and marine pollution, persistent pollutants into ecosystems, climate change, droughts, sea level changes and the spread of disease are the world's major problems today. To overcome this, the Meeting of the American Chemical Society (ACS) in August 2000 approved an alliance between ACS and Green Chemistry Institute (GCI) to build Green Chemistry as a national research priority to harmonize the interests of policy makers, business leaders and the scientific community in new initiative. ACS and GCI in partnership with the International Association of Pure and Applied Chemistry (IUPAC) sponsored the CHEMRAWN XIV World Conference on Green Chemistry, "Towards Environmentally Friendly Processes and Products". The conference brought together leaders of government, industry and academia with the aim of formulating a sustainable development pathway where pollution prevention is used to create a balance between economic development and environmental protection.

Green Chemistry (Green Chemistry / GC) is also called sustainable chemistry, is a philosophy of research and engineering / chemical engineering that advocates the design of products and processes that minimize the use and creation of hazardous compounds [15]. Green Chemistry is the use of chemicals for the prevention of pollution, is the design of chemical products and processes that are environmentally friendly [16]. GC is an approach to overcome environmental problems in terms of the chemicals produced, the process or stages of the reaction used. This concept emphasizes the reduction and use of hazardous chemicals both in terms of design and process. The dangers of chemicals intended in this GC concept include various threats to human health and the environment, including toxicity, physical hazards, global climate change, and depletion of natural resources [17]. Green Chemistry covers all aspects and types of chemical processes to reduce negative impacts on human health and the environment.

The United States Environmental Protection Agency (US-EPA) explains several principles in Green Chemistry, so that various development activities, including industries, still pay attention to "cleanliness" and "health" in pre-production, production and post-production activities. Green Chemistry technology provides a number of benefits including reducing waste, reducing the cost of expensive pipeline maintenance, safer products, reducing energy and natural resource use, and increasing the competitiveness of chemical plants [18]. The development of Green Chemistry will have many positive impacts on living things, the environment, and the increase in the economic sector along
with the increasing development of industry in Indonesia [19]. Green Chemistry has evolved into a major practice supported by academics, industry, and government. GC includes human and environmental health, which is guided by very specific principles of chemical practice. This principle is summarized in the Twelve Principles of Green Chemistry, namely: (1) preventing the emergence of waste; (2) atomic efficiency (efficiency of materials used in the process); (3) design of a safe synthesis process (little toxicity); (4) design of safe chemical products; (5) creating renewable raw materials; (6) catalyst (increased selectivity of reagents and energy use); (7) reducing the derivatization process (minimizing the use of additional reagents); (8) solvents and additives are safe; (9) energy efficiency; (10) design for degradation (chemical products must be designed with consideration of environmental aspects, must be easily degraded and not accumulate in the environment); (11) direct analysis to reduce pollution (analytical methods carried out in real-time can reduce the formation of unwanted by-products, focusing on developing analytical methods and technologies that can reduce the use of hazardous chemicals in the process). (12) minimize the potential for accidents (chemicals used in chemical processes must be chosen in such a way that the potential for accidents can lead to the entry of chemicals into the environment, including explosions, and fires can be avoided). The realization of the 12 basic principles can be done through the use of a curriculum with a Green Chemistry approach [20].

2.3. Development of Ionic Liquid teaching materials

To be able to apply Ionic Liquid material into the vocational curriculum, teaching materials must be made first by adopting the material from science and technology books [21]. The books are adopted so that they can be easily understood by students. It is planned that the adoption of Ionic Liquid teaching materials will be carried out with reference to the Model of Educational Reconstruction (MER) [22], as shown in Figure 2.

![Figure 2](image-url)
science conceptions and content structures from an educational point of view. This first component is described as clarifying subject matter and analysis of the significance of education. Clarification of subject matter illustrates qualitative analysis of content of textbooks and several journals. Analysis of the significance of education illustrates certain rules for pedagogical standards and learning objectives [23]. Analysis of science content needs to be done because university textbooks are generally consumed only by experts (scientists), while for students, presentation of content directly from university textbooks is difficult, so the teaching materials are constructed to be simpler [22].

2.4. Data collection
This study emphasizes the analysis of material requirements for Ionic Liquid teaching materials oriented to Green Chemistry to be delivered to vocational students as the latest material developments that are very useful to be able to be applied through the insertion of these materials into chemical engineering curriculum / syllabus.

Table 2. The questionnaire instrument covered positively aspects of attitude, knowledge and skills.

| No. | POSITIVE STATEMENTS                                                                 | SCORE |
|-----|-------------------------------------------------------------------------------------|-------|
| A   |                                                                                     | VA    |
| 1   | I've heard the term Ionic Liquid (Ionic Liquids / ILs)                                | 5     |
| 2   | Ionic Liquid learning is needed at the polytechnic level as enrichment material      | 4     |
| 3   | Ionic liquid material has actually been around for a long time, but just heard term now | 3     |
| 4   | I am interested in new ionic liquids                                                | 2     |
| 5   | I am willing to study and disseminate in learning this new material as an advance in science & technology | 1     |
| B   |                                                                                     | AN    |
| 6   | Ionic liquids are ionic salts                                                      | 5     |
| 7   | Ionic liquids are liquid at room temperature                                        | 4     |
| 8   | Ionic liquids are green solvents                                                   | 3     |
| 9   | One of the properties of ionic liquids is high steam pressure                      | 2     |
| 10  | Ionic liquids are high-tech materials                                               | 1     |
| 11  | We can synthesize ionic liquids                                                    |       |
| 12  | Ionic liquids are electrolyte                                                       |       |
| 13  | Ionic liquids are ionic compounds                                                   |       |
| 14  | Ionic liquids do not contain solvents                                              |       |
| 15  | The use of ionic liquids will not damage the balance of nature                     |       |
| 16  | The function of ionic salts can be replaced by ionic liquids                        |       |
| 17  | Ionic liquids are organic compounds                                                 |       |
| 18  | There are organic elements in ionic liquids                                         |       |
Table 3. The questionnaire instrument was covered by negative aspects of knowledge.

| No. | NEGATIVE STATEMENTS                             | SCORE |
|-----|-----------------------------------------------|-------|
|     |                                               | VA    | A    | N    | DA   | VDA  |
| B2  | KNOWLEDGE                                     |       |      |      |      |      |
| 19  | Ionic liquids are the same as ionic solutions  |       |      |      |      |      |
| 20  | Ionic liquids are formed from metal cations with non-metallic anions |       |      |      |      |      |

The research sample was taken through purpose sampling technique, namely five lecturers of chemical engineering as respondents in one of the private polytechnics [24]. Two respondents were graduates of chemical engineering master and the other three were master of science graduates who all came from well-known state universities. The research instrument was a questionnaire containing 20 statements with 18 items positive statement items and 2 negative statement items as shown in Table 2 and Table 3. The statement is also divided into two categories, namely 5 items in the form of attitude aspects (statement no. 1-5) and 15 items in the form of knowledge and skills aspects (statement no. 6-20), as shown in Figure 2. The plan is material for Ionic-oriented Green Liquid Chemistry will be given to vocational students especially chemical engineering majors with the aim of increasing the competency of students' knowledge, skills and attitudes related to the planning and processing of chemicals [25].

Data from respondents were collected through questionnaires and measured using a Likert scale with five choices [26]. For a positive statement, a score 5 = SA (very agree / very good / very like), score 4 = A (agree / good / like), score 3 = N (neutral), score 2 = DA (disagree / not good / dislike), score 1 = VDA (very disagree / not very good / strongly disagree). As for negative statements, scores 5 = VDA (very disagree / not very good / strongly disagree), score 4 = DA (disagree / not good / dislike), score 3 = N (neutral), score 2 = A (agree / good / like), score 1 = VA (very agree / very good / very like). The score of the measurement results, then interpreted so that it becomes information that is needed by researchers for the next treatment [27].

3. Results and discussion

The results of filling out and processing positive response questionnaires and negative responses both for attitude, knowledge and cognitive sciences from the five respondents are shown in Table 4. Interpretation of the results of Likert scale questionnaire processing on the five respondents, for five attitude statements, all respondents agreed that Ionic Fluid learning was needed at the Polytechnic as enrichment material, interest and willingness to study and disseminate the material to vocational students reaching 80% with the fifth category of respondents very agree, (very good / very fond). The results of the questionnaire for the statement "have heard the term Ionic Liquid and actually Ionic Liquid material has already existed but have only now heard the term" only reached 76% with the agreed category (good / like), this is possible because respondents experienced a bit of confusion in terms of Ionic Liquids with Ionic Solutions, but in general the average attitude score reached 78.4%, which proves that Ionic Liquid material agrees to be delivered to vocational students [28].

For the results of questionnaire processing on the cognitive and skills aspects of 13 positive statements, the average response score of respondents reached 69.85% with the agree / good / like category on the Ionic Liquid material to be developed. The average score is in the middle level range of 60% - 79.99% with the agree / good / like category. This proves that lecturers' understanding of Ionic Liquid material still needs to be improved.

For negative statements, the average score only reaches 42% with a sufficient / neutral category even approaching the category of less / less agree. This interprets that respondents are still hesitant in understanding Ionic Liquid teaching materials. This is understandable because the teaching materials for Ionic liquids are new material that previously did not exist in the vocational syllabus. To be able to
increase the understanding of respondents, it is necessary to conduct training or technical guidance on Ionic Liquid teaching materials so that respondents can transform their knowledge well to students.

### Table 4. Respondents' positive response processing.

| No. | VA | A | N | DA | VDA | Score (%) | DESCRIPTION                  |
|-----|----|---|---|----|-----|------------|-----------------------------|
| A   |    |   |   |    |     |  76        | agree /good / like          |
| 1   | 1  | 2 | 2 | 5  |     |  80        | very agree /very good / very like |
| 2   | 4  | 1 | 1 | 3  |     |  76        | agree /good / like          |
| 3   | 1  | 3 | 1 | 2  |     |  80        | agree /good / like          |
| 4   | 1  | 3 | 3 | 1  |     |  80        | very agree /very good / very like |
| 5   | 1  | 3 | 1 | 2  |     |  80        | agree /good / like          |

**AVERAGE SCORES (%)**        78.4    agree /good / like

### Table 5. Processing of respondents' negative responses.

| No. | VA | A | N | DA | SDA | Score (%) | DESCRIPTION |
|-----|----|---|---|----|-----|------------|-------------|
| B   |    |   |   |    |     |            |              |
| 6   | 5  |   |   |    |     |  80        | very agree /very good / very like |
| 7   | 1  | 3 | 1 | 1  |     |  72        | agree /good / like          |
| 8   | 1  | 4 |   |    |     |  68        | agree /good / like          |
| 9   | 3  | 2 |   |    |     |  72        | agree /good / like          |
| 10  | 1  | 3 | 1 | 1  |     |  72        | agree /good / like          |
| 11  | 1  | 1 | 3 | 1  |     |  72        | agree /good / like          |
| 12  | 4  | 1 |   |    |     |  76        | agree /good / like          |
| 13  | 1  | 3 | 1 | 1  |     |  60        | agree /good / like          |
| 14  | 3  | 1 | 1 | 1  |     |  68        | agree /good / like          |
| 15  | 1  | 4 |   |    |     |  64        | agree /good / like          |
| 16  | 4  | 1 |   |    |     |  76        | agree /good / like          |
| 17  | 2  | 3 |   |    |     |  68        | agree /good / like          |
| 18  | 1  | 2 | 1 | 1  |     |  72        | agree /good / like          |

**AVERAGE SCORES (%)**        69.85    agree /good / like

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All respondents agree that ionic liquids are ionic salts (response no. 6), but respondents have difficulty responding to negative statements "ionic liquids are the same as ionic solutions" and ionic liquids are formed from metal cations and non-metallic anions, the average response score of respondents is only 42% approached the category of minimum / disagreeing. Respondents answered agreeing to the negative statement, whereas in fact ionic liquids differ from ionic solutions because in ionic solutions there are solvents whereas in ionic liquids there are no solvents but only organic cations and organic anions. Difficulty answering questionnaires is possible because of forgetting to distinguish ionic liquids from ionic solutions. Therefore it is necessary to disseminate Ionic Liquid teaching materials to lecturers and students in the polytechnic environment. Statement no. 12 ionic liquids are electrolyte and ionic salt functions can be replaced by ionic liquids (statement no.16), the average score reaches 76% with the agree / good / like category, this gives an understanding that ionic liquids are electrolyte and can replacing ionic salt functions because they use the term ionic which means identical to the electrolyte. For the statement "there is an organic element in ionic liquids, the respondent answers that there are some who answer strongly agree, agree, neutral and some answer do not agree". This interprets that the respondent's answer is only guessing. But if the scores of the three aspects are averaged, including attitudes (78.4%), positive statements of knowledge and skills (69.85%) and negative statements of knowledge and skills (42%), results obtained at 63.42% with categories agree / good / like with Ionic Liquid teaching materials. This data provides an understanding that respondents are quite interested in ionic fluid teaching materials, willing to study and disseminate vocational students.

4. Conclusion
Green Ionic Liquid teaching materials are new material in the field of education, therefore socialization is needed. The interest and willingness of the lecturer to study and disseminate reached a score of 80%, this means that the lecturer needed the Ionic Liquid material. However, the teacher's understanding score still needs to be improved, so that it is necessary to design an Ionic Liquid teaching material that is interesting and easy to understand by both lecturers and students. Through expected curriculum reconstruction, the teaching materials can be easily conveyed to vocational students as a contribution to improve the competency of planning and processing chemicals.

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