Utilization of Agricultural Waste to Be Bioethanol Sources as a Solvent on Paraffin Wax Crude Oil Issues

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Abstract: Crude oil is a chemical compound of saturated paraffin wax, aromatics, napthane, asphaltic, and resins indeed this material produce wax deposits. Deposition of paraffin has potential to harmful the production due to the existence of blockages, whether partial or the whole of the pipeline. Various techniques have been developed to overcome this problem; one of them is the use of solvents from agriculture waste. Incidentally, the materials are easy to obtained and economical. Based on the Central Bureau of Statistics data, the agricultural waste in Indonesia recorded 5,883,730 tons/year for corn waste, 439,657 tons/year for pineapple skin waste, and 15.8 tons/year for rice husk waste. The potential of agricultural waste can be used as a source of raw materials for manufacturing solvents by using bioethanol by ways of pretreatment, hydrolysis, fermentation, and distillation process. In addition, the result of several past studies shows that bioethanol made from pineapple skin produce 8% of ethanol; bioethanol from corncobs produce 19-22% of ethanol; and bioethanol from rice husk produce 14.4227% of ethanol. Therefore, it means that agricultural waste can be used as a source of bioethanol in manufacture of solvent and could overcome the problem of paraffin wax.

1 INTRODUCTION

The decline in production is an obstacle for the oil and gas industry. Decreasing the rate of oil production in wells will occur over time if the well is produced continuously (Wang et al., 2003). Paraffin is a straight chain consisting of 20 to 40 carbon atoms, paraffin is formed at low temperatures (Taraneh et al., 2008). There are several methods for dealing with paraffin wax, including preventive methods, namely heating methods and chemical methods, one of the most effective methods is using hydrocarbon solvents (Khaibullina et al., 2016). Where one way to reduce paraffin wax is by injection of solvent as a wax inhibitor (Al-Yaari et al., 2011).

Organic waste processing has been widely used, such as: palm shells (Yuliusman et al., ; Yuliusman et al., 2018; Afdhol et al., 2017), tea waste, coffee grounds (Yuliusman et al.,), and inorganic waste from plastic waste (Yuliusman et al.,). Bioethanol can be produced from biomass containing cellulose through various enzymatic processes and fermentation (Hu et al., 2018). Bioethanol production from cellulose waste has been developed, rice husk is one of the renewable raw materials for bioethanol production due to availability and cheap. The production process of bioethanol from cellulose raw materials is very complex so that it involves the preatretment process, hydrolosis and fermentation (Nanssou et al., 2016).

Based on the Central Bureau of Statistics data, the agricultural waste in Indonesia recorded 5,883,730 tons/year for corn waste, 439,657 tons/year for pineapple skin waste, and 15.8 tons/year for rice husk waste. Rice husk contains several organic compounds, namely, lignin, cellulose, hemicellulose, nitrogen compounds, vitamin B and organic acids and contains inorganic compounds in the form of silica (Ebrahimi et al., 2017). For rice husk used as raw material for making ethanol can be seen in figure 1 below.

In table 1 there is a composition of cellulose, hemicellulose and lignin from several agricultural materials, it can be seen that corn stover contains about 30-40% cellulose and lignin content 7-18, where the lignin content can inhibit the hydrolysis process.

According to (Cai et al., 2018) several stages of the biomass process will be carried out to

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Figure 1: Rice husks (Cai et al., 2018).

Table 1: Komposisi Cellulose, Hemicellulose dan Lignin dari Lignocellulosic berbeda (Byadgi & Kalburgi, 2016)

Lignocellulosic	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Miscanthus	40	18	25
Coastal	25	35.7	9-18
Corn Stover	35-40	17-35	7-18
Wheat Straw	30	50	15

produce ethanol, namely pretreatment, hydrolysis and fermentation.

- Pretreatment, Biomass pretreatment is important because to get high ethanol yield. The purpose of the pretreatment is to open the ligninselulose structure so that cellulose is separated from lignin so that it is cellulose(Afdhol et al., 2019).
- Hydrolysis, Hydrolysis is the process of breaking down existing polysaccharides in lignocellulose biomass, namely cellulose and hemicellulose which will be broken down into sugar monomers. Cellulose hydrolysis that is done perfectly will produce glucose. Hydrolysis can be carried out chemically using acid or enzymatically. There are several factors that influence the hydrolysis process, namely the first is carbohydrate content of raw materials, pH of hydrolysis, hidrolysys time, temperature and pressure.
- Fermentation, Fermentation is a microbial activity in food ingredients so that the desired product is produced. Common microbes involved in fermentation are bacteria, yeast and mold. The following are important factors that will affect the ethanol yield and efficiency, that is on microbial physiological conditions added to the media, which depends on the optimal conditions for specific growth of the microbes to be used and environmental conditions during fermentation, namely pH and temperature.

Solvent is a solution that is commonly used in the petroleum world at various uses in their respective fields and outside the world of petroleum as well as many used solvents. In the table below is the use of solvents as paraffin inhibitors or as an inhibitor of paraffin formation, and the classification of solvents is also used as a reference for making solvents in the research that will be conducted.

In table 2 there are several specifications of solvents used as paraffin inhibitors with the type of solvent parasol II, where this table is used as a reference specification for the manufacture of ethanol type solvents.

Table 2: Solvent Specifications.

Parameter	**Information**
Color	Clear
Odor	Aromatic
Physical State	Liquid
Form	Liquid
pH	9
Boiling Point	257° F (125°C)
Flash Point	61° F (16.1°C)
SG	0.8528
Density	0.8527

Oil production wells that are Pertamina EP Region Sumatera Field Lirik by LS-124 (JOB PLP Lirik) has paraffin properties with a fairly high wax content. Paraffin crystals from production oil begin to form at temperatures of $<$ 180°F at 100 ppm, at temperatures below 180°F it will increase to $>$ 100 ppm, so that forming wax crystals will be faster, the presence of paraffin causes a decrease in flow efficiency (FE) due to damage formation so that the productivity index (PI) also decreases. By injecting solvent (Xylene) and surfactant oil production increases from 7 BOPD to 43 BOPD.

Therefore in this study a laboratory analysis was carried out, namely making bioethanol using biomass waste derived from rice husk, corn skin and pineapple skin which will be processed so that it becomes a solvent to be able to inhibitor the occurrence of paraffin deposits. wet oil into wet water which is oil that can flow easily (Priyandono et al., 2007).

2 THE PROBLEM OF DEPOSITION OF PARAFFIN WAX

Paraffin is a mixture of hydrocarbon solid crystals formed from linear or normal chains ranging from C_{20} to C_{30} and consists of n-alkanes, iso-alkanes and naphtenes. Wax is a high molecule of heavy paraffin fraction from crude oil which can be separated below from crude oil pouring points.

In general, there are also two types of wax contained in petroleum. First, microcrystalline wax consists of (n-alkanes) such as C_{20} to C_{50} and Secondly, amorphous waxes consist of mostly isoparaffin and naphthalene such as C_{30} to C_{60} (Abdurrahman et al., 2018).

Deposits paraffin wax can be referred to as the deposition of carbon material, which is insoluble or dispersed by crude oil under normal conditions. Normal conditions for maintaining crude oil in its liquid form when temperature and pressure in the reservoir area are in the range of 70 – 150 °C and 55-103 Mpa (Ridzuan et al., 2016).

Figure 2: effect of wax deposits shown above (a) measuring drilling tubing, (b) intersection of the flow pipe, and (c) on the inside of the pipe.

Paraffin settles can also be caused by the loss of volatile light in a crude oil, where the volatile fraction in the crude oil acts as a solvent for wax. When the fluid of this mixture begins to cool, then each component of the wax will separate (become not dissolved) until finally the wax component which has a high molecular weight will solidify. The event where the first wax crystals are formed at a certain temperature is called the onset of wax crystallization or better known as the cloud point or Wax Appearance Temperature (WAT).

Up to 85% of world oil is affected by paraffin wax which settles and solidifies in the wellbore, in tubing, perforations, pump circuits, and rods, and along the flowlines and pipe line transfer systems (Figures 2a, 2b, and 2c).

3 PARAFFIN WAX CONTROL TECHNIQUES

Deposition of paraffin wax causes equipment failure, upstream and downstream flow congestion, and loss of production, transportation capacity, and storage. Because paraffin deposits are waxed, thousands of wells are closed, many pipelines are clogged, transport vessels are transported out of service, tanks are locked, and refinery equipment is closed at certain times globally, all resulting in loss of income.

In other conditions technically removing deposition of paraffin wax in the review includes: Fused Chemical Reaction, Techniques, Heat Applications, Chemical Additives, Magnetic Fluid Conditioning (MFC) and Microbial Products (Abdurrahman et al., 2018).

3.1 Fused Chemical Reaction

For this method, various chemical substances are used to control waxy oil, such as diesel fuel, xylene, toluene, and naphthalene. These substances are used as solvent to dissolve wax deposit in reservoir and increase the well productivity and reservoir condition. There are two ways to inject solvent, continuous injection and soaking injection. Continuous injection is a method using a special injection pump, which set up on the wellhead. The chemical is injected into the wellbore through the annulus. For the soaking method, a technique utilizing a small pump truck dropped the chemical into the wellbore through the annulus at a particular time (Abdurrahman et al., 2018).

3.2 Tecniques

The practice of pigging is a way in which wax removal is commonly accomplished in the field. With this method, deposited wax is techniques removed by launching a pipeline pig along the line to scrape wax from the walls as it is forced along by the oil pressure. This, however, poses the risk of forming a wax plug downstream from the pig as the scraped wax accumulates and is compressed ahead of the pig. In such an event the pipeline could be lost.

The use of bypass pigs tries to address this problem. When the differential pressure across such a pig becomes too high, because of the accumulation of solid wax and debris ahead of it, the bypass pig allows liquid to flow through it and disperse the accumulated solid ahead. However, there is always the danger that if pigging has to be temporarily suspended due to Mechanical failure, or that if the pigging frequency for a pipeline is not correctly optimized, that the result will be a stuck pig and sizable production losses (Aiyejina et al., 2011).

3.3 Hot Water Method

Hot water is one of method used for maintaining the reservoir temperature. Furthermore, hot water which injected into the wellbore slow down the deposition wax process. It can be applied during completion and production. During completion, hot water is circulated into the annulus using coiled tubing. Then, tubing string is heated to maintain the temperature above the pour point. In terms of production, hot water is being used along with water injection to maintain the pressure and temperature. The hot water collected at the manifold for certain purposes. This technique can also be combined with chemical method in order to prevent the appearance of wax in the wellbore (Abdurrahman et al., 2018).

3.4 Biological Treatment

Biological wax removal methods have also been studied in recent years by researchers such as who developed systems of paraffin-degrading bacterial consortiums with nutrient supplements and growth enhancers for controlling paraffin deposition in the tubular and well bore region and in surface flow lines. Their results showed that their systems were highly effective, eliminating the need for repeated scrapings of wax over a period of several months. These methods are especially important because, if successfully implemented, they have the benefit of providing continuous control of wax deposition in pipelines through constant biodegradation, rather than just providing a very temporary fix (Aiyejina et al., 2011).

3.5 Microbial Method

The subject of this method is to decrease the cloud point or appearance of wax as apparent molecular weight of crude oil. This method used the microorganisms that alter the composition of crude oil through bio-degradation. Crude oil in contact with the microorganism (such as Pseudomonas aeruginosa, Bacillus subtillis, and Bacillus licheniformis) may be degraded directly or break the long chain into short chain.

4 RESULT AND DISCUSSION

Bioethanol making there are several important aspects that must be considered such as sample size, acid concentration, reducing sugar content, stirring speed , temperature and fermentation time this can affect the ethanol content that will be produced.

So in this chapter we will also compare the effect of parameters that affect the results of ethanol from the raw materials of rice husks and corn cobs. The following is a detailed explanation of each of the parameters from each raw material.

4.1 Corn Cobs

During the hydrolysis process, hemicellulose acid is converted to cellulose. The results of the acid hydrolysis process showed that the smaller the size of the corn cobs particles (the bigger the mesh), the better the hydrolysis of the acid. This is shown in Figure 3, the hemicellulose level decreased with the smaller size of the corn cobs particles and the cellulose content increased with the smaller particle size.

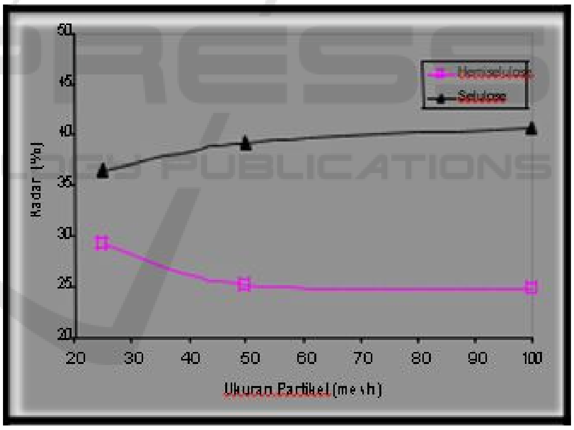

Figure 3: The relationship between material content and particle size during the process acid hydrolysis for 24 hours (Soeprijanto and Prasetyaningrum, 2008).

The effect of particle size on enzyme/acid hydrolysis on glucose conversion is shown in Figure 4. The results showed that the smaller the size of the corn cob particles, the greater the conversion of glucose obtained, because the small-sized particles resulted in having a large contact area between corn cob particles and enzymes/acid so that the process of hydrolysis of enzymes/acid to cellulose to glucose became larger and causing cellulose conversion to increase glucose. The increase in conversion to glucose is also followed by an increase in the dose increase of the enzyme/acid added. With the addition of the highest dose of enzyme 50 ml and various particle sizes (25, 50, 100 mesh), the conversion of cellulose to glucose increased by 43. 19%, 45.69% and 51.01%. So that the highest conversion that can be achieved is 51.01% using the size of 100 mesh corn cobs and 50 ml enzyme doses.

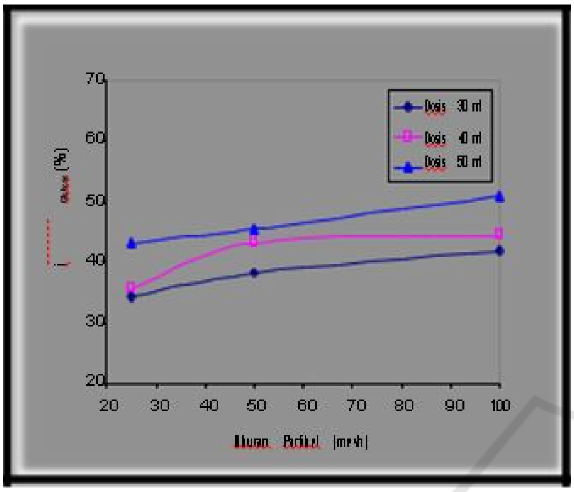

Figure 4: The relationship between glucose conversion and particle size (Soeprijanto and Prasetyaningrum, 2008)

in the hydrolysis process, protons H^+ from HCL compounds will convert fiber groups from raw materials into free radical groups. the free radical group will then be related to the OH^- of H_2SO_4 and produce glucose. when the need for H + from HCL is sufficient to form radical groups from the raw material, the glucose produced is maximal.

As well as the longer the fermentation time, the higher the ethanol produced. this is because the longer the fermentation time, the more glucose is reduced to alcohol, especially ethanol, but of course there is a maximum limit of microbial activity. It can be seen from the result of the graph in figure 5 below (Fachry et al., 2013).

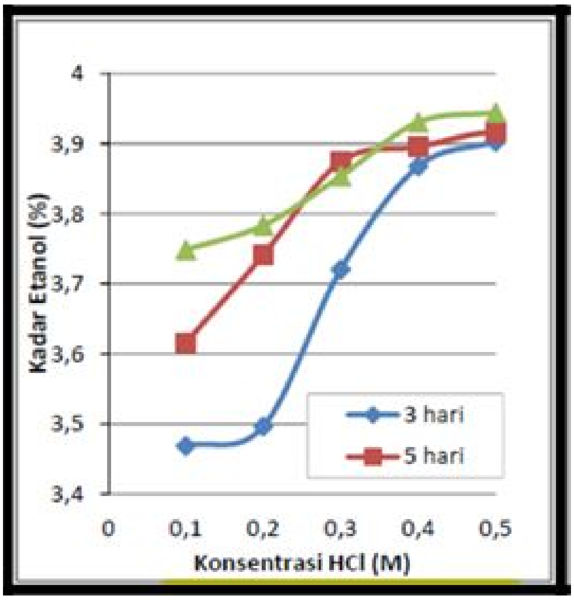

Figure 5: Effect of HCL molarity on ethanol levels at various fermentation times (Fachry et al., 2013)

4.2 Rick Husk

Rice husk has a lot of cellulose content which is around 30% but the lignin content in rice husk is also large, which is around 15% where lignin binds strongly to carbohydrates, so it can inhibit the hydrolysis of cellulose by enzymes. To obtain ethanol from rice husk, the pretreatment stage is needed. The pretreatment stage is done to break the lignin bonds, so that cellulose can be hydrolyzed by enzymes that can produce glucose (Inggrid et al., 2011). One of the pretreatments that can be done is by using alkali peroxide, so that the pretreatment process also adds to costs in the ethanol production process.

At this stage, determining the effect of stirring speed and determining the effect of H2O2 concentration and temperature. Experiments on the effect of stirring speed using 0% H_2O_2 and 2.5% at a temperature of 35°C with variations in stirring speed 0, 100, 150, 200, and 300 rpm. Experiments to determine the effect of H_2O_2 and temperature concentrations were carried out with variations in H_2O_2 concentrations of 0%, 2.5%, 5%, 7.5%, and 10% and temperature variations of 25°C, 35°C, and 45°C.

Experiment on determining the effect of stirring. Stirring uses a paddle because it has the largest cross-sectional area, so that with a small stirring speed can provide a great stirring effect.

When H_2O_2 2.5% 150 rpm cellulose levels should increase because the levels of lignin drop. Because, on a 100% basis when lignin levels decrease (there is lost lignin), the cellulose level rises (even though the amount is fixed). However, in the experiment, the cellulose content dropped because when the lignin bond was tried to be broken, there was some cellulose which was damaged. the effect of variations in stirring, H_2O_2 concentration, and temperature is easier to see when analyzing glucose levels because the changes are greater than changes in lignin and cellulose. Moreover, in the manufacture of bioethanol, which has an important role is the level of glucose.

Based on observation of figure 6 and ANOVA statistical test, stirring has an effect on the level of lignin. At a speed of 150 rpm the level of lignin is lowest because there is no dead zone (at 0 and 100 rpm) and vortex (at 300 rpm), so that radical OH contact with rice husk is good. Good contact results in more broken lignin bonds.

ANOVA statistical test results it can be ascertained that the temperature and H_2O_2 concentration have an effect on the glucose level produced, the higher the concentration of H_2O_2, the higher the glucose produced, but decreases at a 10% H_2O_2 concentration. Meanwhile, changes in operating temperature from 25°C to 45°C do not have a large effect on cellulose levels.

Understanding wax aging mechanisms is also very important to fully understanding the process of the formation of wax deposits in pipelines. Furthermore, understanding these mechanisms and predicting the CCN of particular crude oils would be helpful in determining what chemical inhibitors would be most effective for preventing wax build-up in pipelines carrying those oils.

The continuing research into methods of inhibiting wax deposition and removing deposits has the potential of making the maintenance of crude oil pipelines significantly easier, as it becomes easier to optimize pigging frequency, to determine the minimum pressure required to restart gelled lines, or even to avoid the need for constant wax removal procedures by finding a way to costeffectively implement a promising method of control such as the use of polar crude oil fractions or biological removal measures.

Initial testing of oil containing paraffin wax is very important to determine the wax content contained in oil and the temperature at which wax begins to form. then testing was carried out to test the oil containing paraffin wax after adding a solvent to it, so these two tests were conducted to see the effectiveness of the solvent to overcome the problem of paraffin wax.

As for the tests carried out to identify the content of paraffin wax in oil, which is cloud point testing (ASTM D5771), cold point testing (ASTM D6371) (Products & Products, n.d.) and pour point testing (ASTM D97) (Methods & Oil, n.d.), this parameter can be used as a reference whether the solvent mixed with oil containing paraffin wax can be handled properly or not. and also other supporting tests such as density (ASTM D1298) (Standard, n.d.), specific gravity (ASTM D1250) (Guide, 2004) and ^{0}API (ASTM D287) and viscosity (ASTM D445) (Viscometers et al., 2009). where all these parameters are the reference to the success of the solvent in dealing with paraffin wax.

5 CONCLUSIONS

This work shows how the process of making bioethanol from agricultural waste with optimal conditions such as particle size, enzyme / acid concentration, reducing sugar content, stirring speed, temperature and fermentation time and also in this work provides another alternative in overcoming the problem of oil containing paraffin wax using bioethanol which produced from agricultural waste so that it can prevent environmental damage and provide a more efficient cost alternative in dealing with paraffin wax deposits.

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