Ministry of Environment
and Food of Denmark
Environmental
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SUPERIOR
Development of Glue from non-food Renewable Resources

MUDP report

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1. Introduction

The project SUPERIOR was founded by the Environmental Technology Development and Demonstration Program (MUDP) under the Ministry of Environment and Food of Denmark.

The report represents the primary results and knowledge gained during the project.

The project was carried out in the period December 2017 to September 2018 in a collaboration between Technological Institute, Tønder Forsyning and Bollerup Jensen.

1.1 Purpose

The purpose of the project was to develop a glue system based on non-food/feed proteins combined with inorganic materials such as silicates that are sustainable and a competitive alternative to adhesives containing formaldehyde. The partners' vision is hence to develop and put in place the technical platform for production and sales of fully demonstrated non-toxic industrial glues for wood-based panels, based on the above-mentioned combination. The glues will be formaldehyde-free, fast thermo-curing and environmentally friendly.
The overall aims of the project are to identify and isolate candidate proteins from non-food sources for use in adhesives and from them develop tailored formulations of selected proteins and silicates as formaldehyde-free wood panel glues.

The expected environmental effects of the project are to reduce formaldehyde emission in the environment where glued wood materials are used, significantly. Formaldehyde is a global problem. The emission of formaldehyde takes place both during the manufacturing of the product, in this case wood panel, but also post-product during use. Thus, it is both the producer and the end-user, who are exposed to the emissions.

1.2 Background

There is industrial and societal demand for a new range of non-toxic, sustainable thermosetting adhesives for wood-based panels that can replace and perform as well as current adhesives based on formaldehyde crosslinking of urea, melamine and phenolics. Formaldehyde is a significant problem; in the EU and US it is listed as carcinogenic and its residual emission during use and exposure during manufacture is a serious cause for concern and have severe impact on the indoor climate. The wood industry will hence adopt effective, non-emitting and sustainable alternatives when they become available. Most of the research in renewable glues for the wood sector to date has been undertaken on lignin and tannin-based adhesive systems, or simple unmodified denatured proteins. Most incorporate some formaldehyde or are added in blends to formaldehyde-based glues. These systems are not on the wider commercial market due to relatively poor properties and low durability in the presence of moisture.
Bollerup Jensen (BJ) and the partners have developed a protein-based glue with highly improved properties compared to traditional protein-based glues. The base formulation developed contains partially hydrolyzed soy proteins combined with sili-

cates. However, soy protein is an important nutrient used in both animal feed and human food and is in the longer term not suitable as a basis for large-scale industrial glue production.

Firstly, it is somewhat unethical to remove high nutritional quality proteins from the food chain (analogous to objections to 1st generation ethanol or biofuel production from starch). Secondly, plant proteins used for food and feed such as soy are trending towards raised prices in the near future. Hence, new sources of protein, which are non-food-grade, are needed as low-cost and acceptable raw materials. Several candidate protein sources will be selected and studied in the project covering proteins from e.g.: i) agricultural production side-streams (sugar beet leaves); ii) marine seashore wash-up ('beach cast'); and iii) animal (insect-derived protein coming from larvae grown on municipal and other waste streams that will not be permitted for animal feed or food). These protein candidates have been chosen as they fulfil the following criteria: i) low cost; ii) good availability from stable source and high potential for mass production; and iv) not considered suitable for food/feed.

2. The project

2.1 Work package 1

In work package 1 the focus was to screen, identify and select 4 candidate protein sources.
The objective was to select candidate proteins from quite different types of sources thus it was decided to screen materials from animal (insect-larvae), marine and agricultural sources. We have identified and selected multiple candidate protein sources from various resource streams:

- Insect-larvae grown on municipal waste
- Hatched larvae (Flies) which is a waste from insect production
- Beach cast from the Danish sea shores (marine environment)
- Grass from field cutoffs (agricultural)
- Rape seed cake from production of canola oil (agricultural)
- Brewers spent grains from Beer production (agricultural)

Sourcing of residual biomass materials for extraction of protein sources:

Municipal waste
Initially, an overview (matrix) of available biomasses in Tønder Forsyning and surrounding areas that are not currently applied for other feed purposes, has been compiled. For each biomass, the availability, price, seasonality, and expected applicability as substrate for insect production have been assigned. Based on matrix, the below biomasses were selected for black soldier fly (BSF) production trials:

- Downsized municipal house hold waste
- Spent grains
- Spent grains with different carbohydrate rich byproducts added
- Liquid by-product from the potato starch industry
- Cheese

For each of the experiments, the feed conversion rate (FRC) and size of the larvae were measured as they are of importance for the subsequent LCA-studies. Very promising FCRs (on a dry matter basis) around 2 were obtained for the downsized municipal house hold waste and for the spent grains with different carbohydrate rich byproducts added.
Moreover, a batch of BSF larvae was produced using a composite feed for protein extraction and glue production (set as reference to compare with protein output from other biomasses). By using a commercial composite feed no permission to work with animal-by-products was needed; thus, the produced BSF larvae could be applied directly at Bollerup Jensen and other sites at Danish Technological Institute that are not registered for handling animal by-products.
In addition, the overall production cost of black solider fly has been assessed. The analysis shows that the current prices for the BSF larvae cannot compete with other alternative protein sources applicable for technical applications. Yet it is still unknown if the BSF protein has superior properties compared to other protein sources. Moreover, the adult flies that a currently a by-product from the BSF production may be applicable as a protein source for glue applications. This will be tested shortly in the project.

Insect-larvae

- Frozen Insect-larvae were delivered to Bollerup-Jensen without further processing for testing in the glue formulation. The material and production costs were calculated based on laboratory test and estimated upscaling costs. The assessments indicated that the price for the larvae protein will exceed the maximum cost for an economically feasible glue production based on this protein as source.
- For this reason, hatched larvae (Flies), which is a waste from insect production and thus having no current value will be tested during the coming months.
- Purified protein products were produced from larvae and flies by aqueous extraction, centrifugation and isoelectric protein precipitation. The resulting product was defatted by Soxhlet extraction with diethyl ether to produce protein concentrates from flies- and larvae with 77.5 % and 55.8 % protein, respectively.

Beach cast

- Beach cast was collected from the beaches on Lolland-Falster during the late summer of 2017. The biomass was sorted to remove sand, stones and mussels, and then dried for storage and later dry milling in a hammer- and disk mill prior to aqueous extraction of proteins by further mechanical and enzymatic treatment to generate a protein enriched product with 15.0 % protein.

Rape seed

- Rape seed protein concentrate (55 % protein) was produced using an enzymatic hydrolysis processing method. Rape seed meal was mechanically and enzymatically processed followed by centrifugation and protein coagulation at high temperature.

Brewers spent grains

- Protein concentrate were produced by aqueous extraction with mechanical and enzymatic treatment, sieving, centrifugation. The collected protein paste was spray dried to produce a dry protein powder concentrate of brown color containing 47.4 % protein.

Grass protein from field cutoffs

- The grass protein was collected from the grass protein extraction pilot plant at Aarhus University Foulum.

2.2 Work package 2

Glue Formulation

The proteins have been prepared in two different ways:

- For gluing two pieces of wood together, the protein was mixed with silicate. This type and glue are tested on veneering

- For gluing wood fibers, the protein was chemically degraded in sodium hydroxide. After 1 week, the protein solution is mixed with water glass. This type of glue was used to produce MDF boards and insulation boards.

Testing the glue on veneering was performed by applying 120 g / m2 (industry standard) on a regular particleboard. Leaving the glue open for 1 minute, laying a standard beech on top, leaving it there for 1 more minute. Finally curing the glue in a hot press at 90 C to 130 C for between 30 sec to 2 minutes. After pressing the veneered particleboard rested to the day after to make sure, it was totally cured. The glue strength was evaluated by trying to rip off the veneer. Perfect gluing should break the veneer at the edge of the board.

For gluing wood fibers for MDF or insulation boards the protein is degraded to amino acids / shorter peptide chains. This solution is mixed with silicate. This has earlier with casein proven a good glue for insulation boards. For insulation boards the glue was mixed with wood fibers, pressed to 150 kg/m3 and cured with steam and hot air. Several trails with different hot air temperature and different steam periods was made in order to cure the different gluing systems. Only casein turned out to be able to produce a reasonable board.

For MDF boards the same gluing system was used, but instead pressed in a double-sided hot press at 200 C for 2 min / mm board thickness. Again, casein was the only protein source able to produce a reasonable board.
We were during this work package not able to find an alternative sustainable protein for gluing.

However, we have a silicate glue developed outside this project, which outperform our earlier protein glue system.

Performance Testing

Factory parameters for producing MDF, HDF, particle boards, plywood boards and insulation boards have been studied in order to be able to reproduce these parameters on lab scale. A pilot plant for producing insulation boards have been established. Full performance testing after ISO standards have not been performed as we have no suitable protein candidates for a gluing system.

Pressing with different temperatures and pressing times it is possible to determine the curing speed at each temperature. Soy and casein protein were used as reference as a silicate glue without any protein.

Result: Only rapeseed protein was able to glue the veneer acceptable and this only at a higher temperature and a longer curing time than soya protein. The silicate glue was by far the best glue for veneering.

Pict 1

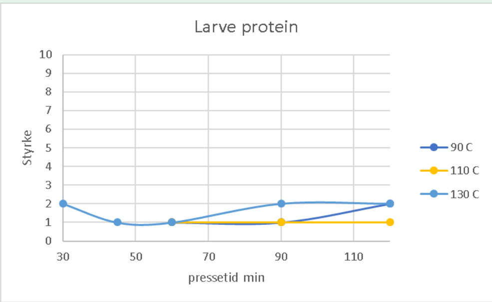
Pict 2

Pict 3

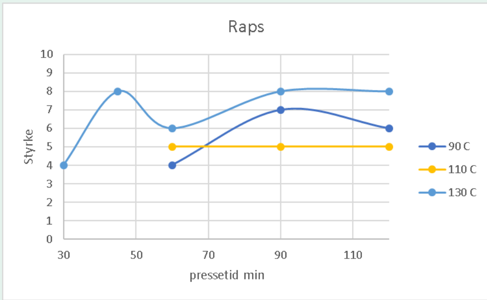
Pict 4

The test method is displayed in picture 1 – 4. Picture 1 is just after pressing the veneer, picture 2 is an almost perfect strength of the glue, given a score of 9. Picture 3 is a relatively good, given a score of 7. The veneer is still breaking, but not at the edge as is optimal. Picture 4 shows a week glue bond given a score of 3. In order to get a score of 1 or 2 the veneer will fall of after pressing the veneer.

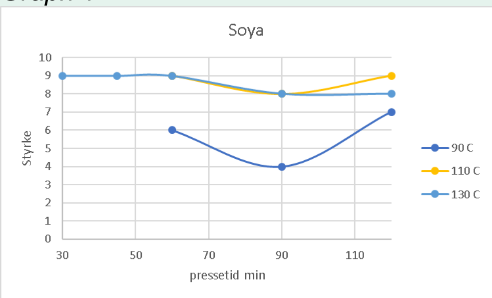
After evaluating all veneers, graphs can be drawn for each glue formulation and pressing temperature, having pressing time at the x-axis and glue strength at he y-axis.



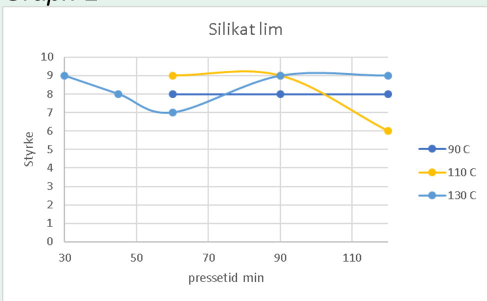
Graph 1



Graph 2



Graph 3



Graph 4

Graph 1 shows the strength of protein extracted from black soldier larvae. The veneer fell of the particleboard right after pressing the veneer. It was not possible to get any strength in the glue. Graph 2 shows rapeseed protein, the alternative protein which showed the best strength. Compared to soy protein in graph 3, soya has full strength at 110 ºC at 30 sec pressing time, where rapeseed needs 130 ºC at 90 sec pressing time, and the strength is not optimal at that pressing time and temperature. The best result we have obtained is a glue without protein displayed in graph 4. Here we have full strength at 90 sec at 90 ºC or at 110 ºC after 30 sec.

Pict. 5

A picture of a produced insulation board is shown in picture 5. The strength were not optimal, as the corner easily broke off. The shown in picture 5 is the best result of the alternative proteins. Only casein was able to produce a board with reasonable strength.

3. Conclusion

As shown in the tests performed in work package 2, casein was the best protein source, for producing an adhesive for insulation boards. For veneering the soya protein gave the best adhesive and even an adhesive without any protein gave better results. With these results, we were unable to identify an alternative protein source, which could perform better than the already known food source proteins.
As a consequence of the lacking results, we had to close down the project after work package 2, because it didn´t make sense to continue the project.

SUPERIOR – Development of Glue from non-food Renewable Resources

Formålet med dette projekt var at udvikle lime baseret på proteiner fra non-food. Limene skulle anvendes i industriel skala til limning af træbaseret plader, og fungere som bæredygtige, non-toksiske alternativer til klæbemidler indeholdende formaldehyd. Det overordnede mål for projektet var at identificere og isolere proteiner fra non-food kilder der kan bruges i limene, og dernæst udvikle kombinationer af proteiner og silikater til lime. Projektet har undersøgt potentielle proteinkilder fra sidestrømme fra landbrugsproduktion, maritimt opskyl ("beach cast") og insektproduktion på affaldsstrømme. Test har vist, at ingen af limene baseret på de undersøgte proteinkilder har kunne opnå samme resultater som lime baseret på sojaprotein eller lime uden proteiner. Dermed er det ikke lykkes at identificere en alternativ proteinkilde, hvorfor projektet er stoppet.

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