Ceres, Inc. and CHOREN USA, LLC

Final Report

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Evaluation of the Relative Merits of Herbaceous and Woody Crops for Use in Tunable Thermochemical Processing GO18083

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EXECUTIVE SUMMARY

This report summarizes the work and findings of the grant work conducted from January 2009 until September 2011 under the collaboration between Ceres, Inc. and Choren USA, LLC. This DOE-funded project involves a head-to-head comparison of two types of dedicated energy crops in the context of a commercial gasification conversion process.

The main goal of the project was to gain a better understanding of the differences in feedstock composition between herbaceous and woody species, and how these differences may impact a commercial gasification process. In this work, switchgrass was employed as a model herbaceous energy crop, and willow as a model short-rotation woody crop.

Both crops are species native to the U.S. with significant potential to contribute to U.S. goals for renewable liquid fuel production, as outlined in the DOE Billion Ton Update (http://www1.eere.energy.gov/biomass/billion_ton_update.html, 2011). In some areas of the U.S., switching between woody and herbaceous feedstocks or blending of the two may be necessary to keep a large-scale gasifier operating near capacity year round.

Based on laboratory tests and process simulations it has been successfully shown that suitable high yielding switchgrass and willow varieties exist that meet the feedstock specifications for large scale entrained flow biomass gasification. This data provides the foundation for better understanding how to use both materials in thermochemical processes. It has been shown that both switchgrass and willow varieties have comparable ranges of higher heating value, BTU content and indistinguishable hydrogen/carbon ratios.

Benefits of switchgrass, and other herbaceous feedstocks, include its low moisture content, which reduce energy inputs and costs for drying feedstock. Compared to the typical feedstock currently being used in the Carbo-V® process, switchgrass has a higher ash content, combined with a lower ash melting temperature. Whether or not this may cause inefficiencies in the process, needs to be verified by long term test runs. Currently, there are not sufficient operational test data available for the Carbo-V® process for the utilization of higher ash content feedstocks.

The application of currently evolving biomass pretreatment technologies, such as pelletization and torrefaction, will be able to expand the portfolio of biomass varieties and species acceptable in gasification processes. Tests showed that 6 mm diameter pellets of switchgrass were superior to 8 mm diameter pellets produced in a flat dye press, and that torrefaction of switchgrass produced an excellent (but currently costly) feedstock that could be handled, crushed, and combusted in a manner compatible with any coal-fed gasification facility.

Ceres will use this information in the development of high yielding, dedicated energy crops specifically tailored for thermochemical conversion. CHOREN will make use of the information for improvement or development of low cost, highly efficient biomass gasification processes that convert a wide variety of biomass feedstocks to fuels, chemicals, heat and power via the production of tar free green syngas on an industrial scale.

BACKGROUND

Thermochemical processes that convert biomass to high quality syngas via gasification are often believed to be universal in their ability to handle a wide range of biomass feedstocks. While this may be true, processing efficiency, yield and profitability may change significantly when switching between herbaceous and woody feedstocks if process conditions are not changed to accommodate the different feedstock materials. Other parties have performed significant analytical, field and laboratory testing in characterizing harvest and feed systems for a variety of biomass types, with the goal of providing robust feed systems capable of processing diverse feedstocks. The majority of work has focused on producing a uniform and chemically homogenous biomass feed for sugar-based biochemical conversion systems, with corn stover receiving the most attention to date. Little or no work has been performed to date addressing the consequences of diversification of feedstock species or the optimization of a range of plant systems (woody vs. herbaceous, annuals vs. perennials) for thermochemical systems. As a result, little or no large-scale thermochemical testing of biomass supplies has been possible. Adjusting process conditions for optimum product yield or steady state production may be necessary to keep large-scale gasifiers operating year round at full capacity and maximum profitability. This project includes an initial evaluation of the magnitude of adjustments that may be required for near-optimal processing of dedicated herbaceous and woody energy crops in a single thermochemical facility. The data generated in this project will also guide the development of biomass feedstocks that will consistently meet industrial specifications for conversion to liquid fuels using thermochemical processes.

First year activities focused on understanding feedstock variability in both composition and thermochemical properties and the relationship between chemical and thermochemical properties in these feedstocks. Second and third year activities explored process optimization and gather information on the potential economic impacts of feedstock variability on thermochemical processes.

The project was concluded on budget and more tests had been performed than initially planned due to strict cost control measures, intelligent use of financial resources and the no-cost extension time period granted by the DOE. Additional information on task activities, including data, results and plans for a way forward is included in the final report that follows.

WORKPLAN

The three-year project work plan (originally two years plus a one year no-cost extension) and progress in year 1 to year 3 is outlined in Table 1.

	Start Date	**End Date**	**Status**	**Completed**
Task A: Sample screening and Selection	1-Jan-09	27-Aug-09	Done	**X**
A.1. Switchgrass	1-Jan-09	31-Mar-09	Done	**X**
A.2. Willow	1-Jan-09	27-Aug-09	Done	**X**
Task B: Characterization of Samples	1-Jan-09	16-Oct-09	Done	**X**
B.1. Chemical Characterization	1-Jan-09	16-Oct-09	Done	**X**
B.1.1. Switchgrass	1-Jan-09	30-Jun-09	Done	**X**
B.1.2. Willow	1-Jan-09	30-Dec-09	Done	**X**
B.2. Thermochemical Characterization	1-Jan-09	16-Oct-09	Done	**X**
B.2.1. Switchgrass	1-Jan-09	30-Jun-09	Done	**X**
B.2.2. Willow	1-Jan-09	30-Dec-09	Done	**X**
Task C: Data Analysis and Thermochemical Process Testing	15-Sep-09	30-Mar-10	Done	**X**
C.1. Data analysis and Report	1-Oct-09	30-Mar-10	Done	**X**
C.1.1. Report on relationship between chemical and thermochemical properties	23-Oct-09	30-Mar-10	Done	**X**
C.2. Sample Selection	1-Mar-09	30-Mar-10	Done	**X**
C.2.1. Selection of samples for additional testing	2-Mar-09	30-Mar-10	Done	**X**
C.2.2. Transfer of selected SWG samples to CHOREN	30-Mar-09	15-Apr-10	Done	**X**
C.2.3. Transfer of selected Willow samples to CHOREN	30-Mar-09	15-Apr-10	Done	**X**
C.3. Thermochemical Process Evaluation	15-Apr-09	31-Oct-10	Done	**X**
Task D: State of Technology Assessment	2-Nov-09	31-Dec-11	Done	**X**
D.1. Feedstock Optimization	1-Mar-10	30-Mar-11	Done	**X**
D.1.1. Select bulk samples for preprocessing tests	1-Oct-10	31-Dec-10	Done	**X**
D.1.2. Transfer of bulk feedstock samples to CHOREN	1-Nov-10	30-Mar-11	Done	**X**
D.1.3. Small scale thermochemical analysis of Miscanthus and Sorghum	1-Mar-11	30-Jun-11	Done	**X**
D.2. Feedstock Preprocessing	1-Jan-11	30-Sep-11	Done	**X**
D.3. Thermochemical process simulation	1-Apr-11	30-Sep-11	Done	**X**
D.4. Data analysis and report	1-Jul-11	30-Oct-11	Done	**X**
Final Project Report	1-Nov-11	15-Nov-11	Done	**X**

Table 1. Project timeline and progress

* Table has been updated based on the no-cost extension of the project.

TASK A: SAMPLE SCREENING AND SELECTION

TASK A1: SWITCHGRASS

The first experimental task (year 1) involved screening of a wide variety of feedstock samples from willow and switchgrass species to select a set of samples that represent variations in yield, chemical composition, thermochemical parameters, geography, environment, storage conditions, etc. likely to be seen in these feedstocks within the U.S. The switchgrass variability screen selected 100 samples from over 3,000 available switchgrass samples in the Ceres archives. These archives include samples from partners, collaborators and internal field trials. The 100 switchgrass samples were grouped into two experimental sets.

- **G-series Switchgrass:** Selected to explore genetic diversity. The G-series consisted of 45 samples representing over 30 accessions grown in a single location in Oklahoma under identical management conditions. Upland and Lowland ecotypes were evenly represented with 20 upland, 20 lowland and 5 samples of unknown ecotype. All samples were hand collected from mature stands (15 + years). To assure that all varieties and ecotypes were in full senescence, samples were harvested in late January.
- **E-series Switchgrass:** selected to explore genetic, environmental and management effects. The E-series consisted of 55 samples representing 38 accessions grown in 14 locations under a variety of management practices, harvest methods and harvest dates. Thirty-one of the E-series samples were of lowland ecotype and the remaining 14 were upland ecotypes. Maturities varied with 45 samples from first year stands, 4 samples from second year stands and 6 samples from mature stands.

TASK A2: WILLOW

The willow variability screen was performed by a commercial partner to represent the compositional variability expected in willow energy feedstocks available in the Eastern United States. An additional 10 samples were provided by CHOREN to represent feedstocks currently being used in their Beta facility in Freiberg, Germany.

- **U.S. Willow:** The U.S. Willow collection included 51 samples of willow coppice samples managed under commercially relevant conditions obtained from the State University of New York (SUNY). The samples included 12 species of Salix and 18 hybrid crosses. Samples from 12 locations were harvested in December 2008. Two maturities are represented with 15 first year samples and 36 third year samples.
- **DE Willow:** The German willow samples were all second year samples grown in a single location under commercially relevant conditions. The DE Willow set includes 10 species harvested in January 2009.

Near Infrared spectra were collected for all samples using a Bruker Optics model MPA Fourier Transform Near-Infrared (FT-NIR) Spectrometer with an integrating sphere and a rotating sample cup assembly. This instrument has a standard lead-sulfide detector array that monitors NIR light from 12,800 – 5,800 cm^{-1}. Sample selection was aided by multivariate analysis using Unscrambler© software by CAMO, Inc. and OMNIC© software by Bruker Optics.

TASK B: CHARACTERIZATION OF SAMPLES

TASK B1: CHEMICAL CHARACTERIZATION

The chemical composition of each sample was determined using high-throughput, independently calibrated compositional analysis methods developed and validated at Ceres. These unique methods are capable of quantifying more than 95% of the dry mass of biomass samples, including ash, extractives, lignin, protein, glucan, xylan, arabinan, mannan, and acetic acid. The Ceres composition methods have been calibrated relative to NIST Standard Reference Materials and standard wet chemical methods developed at NREL for biomass conversion applications. The mass closures were 100.5 ± 4.0 % (95% C.I.) for switchgrass samples and 94.9 ± 3.6% (95% CI) for willow samples. Glucuronic acids were not measured on the willow samples, but the expected ranges of 3-6% bring the mass closure to around 100%. Compositional ranges for all constituents are shown in Table 2.

The experiment as designed provides information only about the ranges expected for each constituent, but no information about the distribution of a representative population. Figure 1 shows a histogram of the lignin contents measured in the G-series and E-series samples. The individual bars are spaced to reflect chemically distinguishable values, to illustrate that nearly all levels in the range are represented in this evaluation. The multivariate analysis methods used in sample selection provided experimental samples sets that represented the maximum number of concentration levels with the minimum number of samples. The height of each bar shows the frequency of that value in the experimental samples.

	Range (% dry wt)			
Constituent	SWG G-series	SWG E-series	US Willow	DE Willow
Extractives	5 -10	9 - 30	9 - 14	6 - 11
Ash	2 - 7	1 - 7	1 - 3	1 - 2
Sucrose	1 - 4	1 - 8		
Lignin	18 - 22	11 - 21	23 - 29	21 - 25
Glucan	30 - 39	19 - 38	32 - 39	37 - 41
Xylan	21 - 25	20 - 24	11 - 14	14 - 16
Galactan			1 - 2	1 - 2
Arabinan	3 - 4	3 - 4	1 - 2	1 - 2
Mannan			1 - 2	2 - 4
Protein	0.3 - 2	1 - 5		
Acetyl	3 - 4	2 - 3	2 - 6	3 - 5
N	45	55	51	10

Table 2. Compositional Variability in Experimental Samples

More variability was seen in the E-series switchgrass than the G-series switchgrass. This was particularly noticeable in the ash, protein, lignin and glucan content. These differences likely reflect differences in maturity of samples collected and the soil on which the samples were grown. As expected, the non-structural components, extractives and sucrose were higher in switchgrass than in willow, as were hemicellulose levels (Xylan). Lignin concentrations were higher in willow.

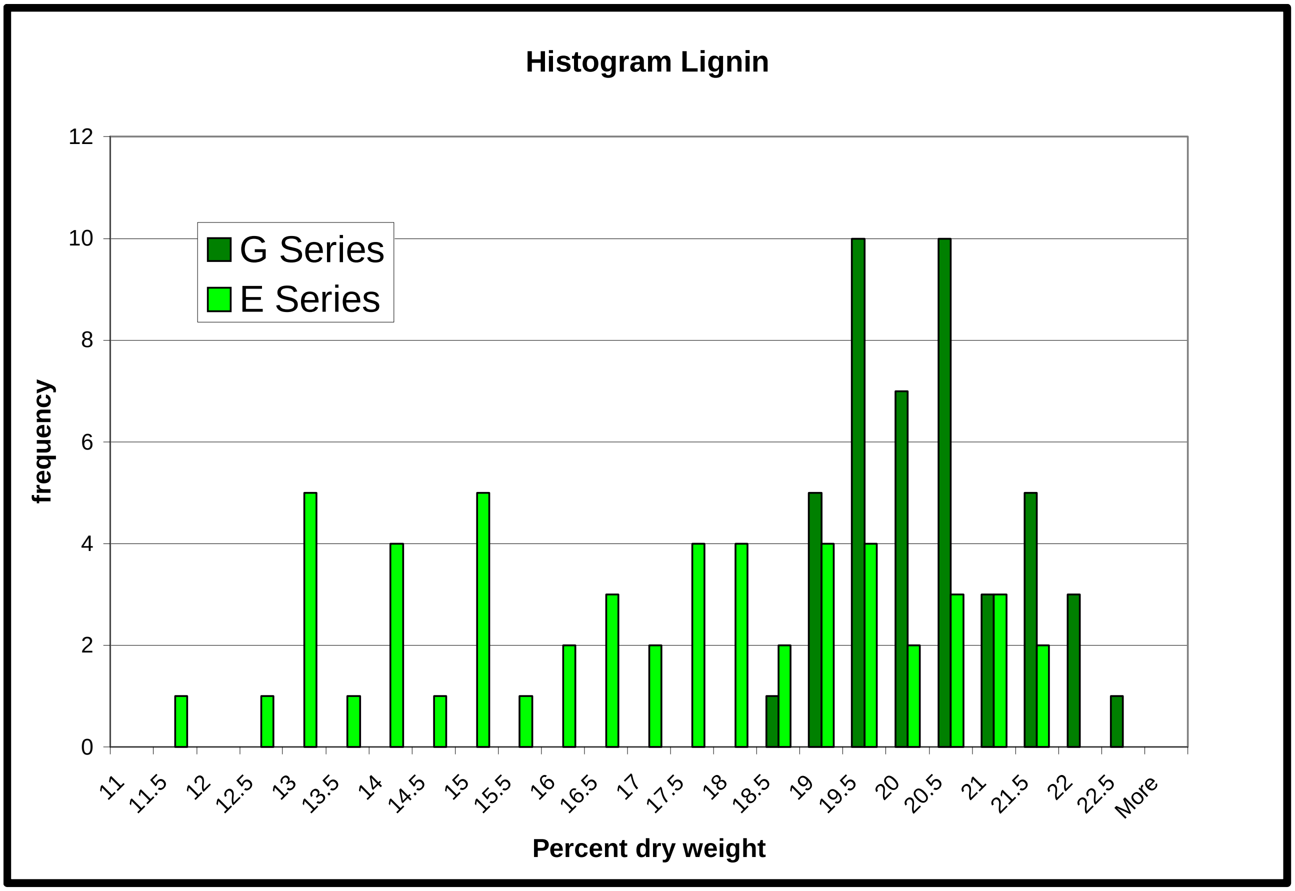

Figure 1. Histogram of lignin values in E-Series and G-series switchgrass samples

TASK B2: THERMOCHEMICAL CHARACTERIZATION

The selected samples were also characterized for thermochemical parameters including BTU analysis (higher heating value, HHV), Ultimate analysis (C, H, N, S, O, Ash, and moisture), and Proximate analysis (moisture, ash, volatile matter and fixed carbon). All thermochemical analyses were performed according to ASTM standard methods.

The ranges seen in the thermochemical properties of each of the experimental sets are shown in Table 3. In general, willow and switchgrass were shown to have similar thermochemical properties.

	Range			
Measurement	**SWG G-series**	**SWG E-series**	**US Willow**	**DE Willow**
Carbon (%)	46.0 - 48.0	44.0 - 49.1	47.8 - 49.9	48.6 - 49.3
Oxygen (%)	41.2 - 45.0	39.6 - 44.5	42.6 - 44.4	43.8 - 44.9
Hydrogen (%)	5.5 - 5.9	5.5 - 6.0	5.9 - 6.3	5.9 - 6.0
Nitrogen (%)	0.2 - 0.4	0.2 - 1.9	0.3 - 0.7	0.2 - 0.4
Sulfur (%)	0.04 - 0.08	0.03 - 0.19	0.02 - 0.06	0.02 - 0.04
Volatiles (%)	77.4 - 83.7	73.7 - 82.4	77.3 - 80.7	78.8 - 82.5
Fixed Carbon (%)	11.8 - 16.9	13.9 - 18.9	17.7 - 20.7	12.0 - 16.1
Ash 750ºC (%)	3.1 - 7.0	2.1 - 10.3	1.1 - 2.6	1.1 - 1.5
HHV (BTU/lb)	7731 - 8062	7508 - 8284	8171 - 8639	8215 - 8326
Chlorine (µg/g)		1760 - 6890	10 - 98	24 - 56
N	45	55	51	10

Table 3. Themochemical Variability in Experimental Samples

The range of HHV values seen in switchgrass demonstrates that the energy content of this dedicated energy feedstock is at the high end of ranges reported in the DOE database for herbaceous materials (http://www1.eere.energy.gov/biomass/feedstock_databases.html) and within the ranges reported for woody feedstocks. All of the measured thermochemical parameters were within expected ranges for these feedstocks.

The ash measurements performed according to the thermochemical methods reported slightly higher values than the compositional methods because wet chemical methods report only structural ash and the thermochemical methods include water-soluble salts that are counted as extractives in the compositional methods. The effect of the soluble salts found in switchgrass on ash melting behavior was not known so a full ash characterization was also performed. Table 4 shows the concentration ranges for ash components.

Wt% in Ash	SWG G Series	SWG E Series	Willow US	Willow DE
Al as Al_2O3	0.3 - 0.9	0.1 - 2.6	0.1 - 0.7	0.1
Ca as CaO	6.0 - 12.3	5.9 - 23.7	35.6 - 71.5	27.5 - 41.7
Fe as Fe_2O_3	0.2 - 0.4	0.1 - 2.8	0.1 - 0.5	0.1 - 0.2
K as K_2O	0.7 - 9.8	2.7 - 31.0	11.1 - 25.7	24.1 - 32.8
Mg as MgO	2.0 - 7.0	3.4 - 22.1	2.1 - 6.9	3.8 - 6.1
Mn as MnO	0.0 - 0.1	0.0 - 1.1	0.1 - 1.4	0.2 - 1.3
Na as Na_2O	0.1 - 2.0	0.1 - 4.1	0.1 - 0.9	0.1 - 0.3
P as P_2O5	1.7 - 8.4	1.2 - 10.3	4.6 - 16.8	9.9 - 15.8
Si as SiO_2	58.8 - 78.8	18.4 - 74.7	0.3 - 3.4	0.3 - 0.8
Ti as TiO_2	0.0 - 0.1	0.01 - 0.20	nd	nd
S as SO_3	1.5 - 5.8	1.7 - 11.0	3.5 - 11.5	3.4 - 6.7

All values are reported as percent dry weight of ash

Table 4. Ash analysis for the experimental samples

The relative abundance of the ash components determines the ash melting point and slagging behavior. Major differences in the concentrations of calcium, potassium, phosphorus and silica in switchgrass and willow suggest that accommodating differences in the thermochemical behavior of ash will be important for a tunable process using both feedstocks.

TASK C: DATA ANALYSIS AND THERMOCHEMICAL PROCESS TESTING

TASK C1: DATA ANALYSIS AND REPORT

One of the main goals of this project was to enhance our understanding of the relationships between chemical and thermochemical properties in switchgrass and willow. The first evaluation was a comparison of the Hydrogen-to-Carbon ratios in the samples. The H/C ratios calculated as mole percents are shown in Table 5.

	Range H/C (molar)
SWG G-series	1.41 - 1.51
SWG E-series	1.39 - 1.53
US Willow	1.43 - 1.47
DE Willow	1.45 - 1.53

Table 5. H/C ratios for switchgrass and willow experimental sets

Given the composition data, a much greater difference in H/C ratio had been expected. The sum of cellulose and hemicellulose in switchgrass was as high as 71% in switchgrass samples. The highest value measured in the willow samples was only 61%. Measured lignin contents in willow were 5-12% higher than those measured in switchgrass. The hydrogen-to-carbon ratio in carbohydrate polymers is typically 1.7 times higher than that seen in lignin (Biomass Glossary 2007), suggesting that increasing carbohydrate content could be a path to increasing hydrogen content in feedstocks. The mass percent of carbon in lignin is around 62% while percent carbon in carbohydrate polymers is only 40%, suggesting that the H/C ratios should be very different for these feedstocks. Further analysis of the data revealed a possible explanation. The hypothesis failed to take into account the presence of 3-6 % (w/w) uronic acids normally found in willow that will raise the measured H content. Further complicating the discussion is the presence of ferulate and para-coumerate esters in the measured switchgrass lignin, which will lower the measured carbon content. *The net result is an indistinguishable difference in the H/C ratios for theses feedstocks.* However, the thermochemical profiles of cellulose, hemicellulose and uronic acids are likely to be very different as are those of true lignin and the aromatic esters found in grasses. The real benefits of switching to herbaceous feedstock will be revealed not in measured H/C ratios but in the relative concentrations of the underlying polymers and their thermochemical kinetics and product ratios.

The next evaluation looked for significant correlations between compositional and thermochemical parameters. In this exercise, the data was evaluated using The Unscrambler multivariate analysis software by Camo. The average and standard deviation for each constituent or parameter was calculated. Standard deviations were compared to known method errors and only those parameters with a standard deviation more than twice the method errors were evaluated. Each of the four experimental sets was evaluated as a separate population. Prior to generation of the correlation matrix, each parameter was z-scored and mean centered to allow correlation across different measurement units and concentration ranges.

Constituent	Correlations Coefficient
Glucan EF	0.627
Total Carbohydrates	0.621
Sulfur	0.588
Carbon	0.868
Hydrogen	0.805
Potassium	0.619
Silica	-0.508
Volatile Matter	0.624

Table 6. Summary of important correlations between HHV and other parameters in the Switchgrass G-series samples.

A summary of the cross correlation coefficients for the G-series switchgrass set are shown in Table 6. Correlation coefficients greater than 0.6 were considered to be significant for this exercise. As expected, the main contributors to HHV are carbon and hydrogen content. Carbohydrates, the main source of carbon and hydrogen, are also correlated with HHV. An unexpected correlation with volatile matter was also seen. These results are consistent with our hypothesis that sufficient diversity exists in important chemical and thermochemical properties and that diversity may be tapped to improve switchgrass feedstock for thermochemical processing.

When the same exercise was performed with the E-series switchgrass group, nearly all constituents show variability relative to the methods errors. In spite of the high variability, fewer correlations were seen between individual parameters. As expected strong correlations were seen between HHV and Total Carbon (0.992) and both carbon and HHV were correlated with volatile matter with correlations greater than 0.7. Also for the willow sample sets, similar strong correlations were seen between HHV, carbon and hydrogen.

TASK C2 AND C3: SAMPLE SELECTION AND THERMOCHEMICAL PROCESS EVALUATION

A set of 10 samples of switchgrass and 10 samples of willow were analyzed in Germany by SGS Institut Fresenius. The results showed that the main differences of switchgrass as a herbaceous species versus woody biomass species are in the higher ash contents and the lower ash melting temperature of the switchgrass samples. In terms of elemental composition, both types of biomass are similar, except for higher values of sulfur and chlorine present in the switchgrass samples.

From these sets, three different varieties were selected for the ensuing preprocessing tests and those selected samples were shipped to Europe. A brief summary of the comparison between the selected switchgrass samples and willow samples on their elemental analysis and suitability for the Carbo-V® technology is shown in Table 7. Qualitative comparison of switchgrass and woody biomass regarding ash composition, ash characteristics, and their potential effects in the CHOREN Carbo-V® process.

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Parameter	Switchgrass vs base case (wood)	Impact
C	Comparable	Negligible
H	Comparable	Negligible
O	Comparable	Negligible
N	Comparable	Negligible
S	⬆	Minor impact on downstream units
Cl	⬆	Some impact on downstream units
Moisture content	⬇	High cost of drying wood
Ash	⬆	High
Ash melting temperature	⬇	High

Table 7. Qualitative comparison of switchgrass and woody biomass regarding ash composition, ash characteristics, and their potential effects in the CHOREN Carbo-V® process.

The two separate species differ mostly in their sulfur and chlorine content as well as in their ash content, ash melting temperature and moisture content. While switchgrass can be harvested at a very low and desirable moisture content, willow needs to be technically dried before acquiring the desired moisture content of 15 percent for the Carbo-V® gasification process. Compared to the typical feedstock currently being used in the Carbo-V® process, switchgrass has higher ash content, combined with a lower ash melting temperature. Whether or not this may cause inefficiencies in the process, needs to be verified by long term test runs. Currently, there are not sufficient operational test data available for the Carbo-V® process for the utilization of higher ash content feedstocks. The main purpose of future tests would be to ascertain the optimum process parameters in order to efficiently convert such a higher ash feedstock.

TASK D: STATE OF TECHNOLOGY ASSESSMENT

TASK D1: FEEDSTOCK OPTIMIZATION

A total of 9 tons of switchgrass consisting of 3 replicates of 3 varieties (EG1101, EG1102, and EG2101) were prepared by Ceres and shipped to CHOREN. Along with the switchgrass samples, 200 kg of high biomass sorghum (ES5200) were prepared for CHOREN analysis. Both switchgrass and high biomass sorghum samples were shipped to CHOREN, Germany and arrived for the Feedstock Preprocessing tests.

As an additional task for feedstock optimization, 20 Miscanthus, 6 Switchgrass, 10 Sorghum varieties were prioritized for thermochemical analysis. Ultimate analysis with direct-O (% compositions of C, H, N, O, and S), proximate analysis (% compositions of volatiles, fixed carbons, and ash), and higher heating value (BTU/lb) were measured and summarized in Table 8. While there are some minor variations among individual lines, all three sorghum, switchgrass, and miscanthus show comparable data on both ultimate and proximate analysis. In BTU analysis, all three showed significant overlapping ranges around 8000 BTU/lb, but in general, sorghum was lower and switchgrass trended higher. Since these samples have been grown and collected from multiple locations, it is reasonable to assume that environment and soil could be the main cause of large variations on ash composition. Most of the elements measured had more than several fold differences.

Measurement		Sorghum	Switchgrass	Miscanthus
Ultimate with direct O (%w / w dry biomass)	C	44.8 ~ 47.8	45.8 ~ 48.9	46.2 ~ 47.8
	H	5.5 ~ 6.1	5.5 ~ 6.0	5.5 ~ 6.0
	N	0.1 ~ 1.0	0.2 ~ 0.6	0.3 ~ 1.0
	O	42.1 ~ 45.5	41.2 ~ 44.1	41.4 ~ 43.6
	S	0.1 ~ 0.1	0.0 ~ 0.1	0.1 ~ 0.1
Proximate analysis (%w / w dry biomass)	Volatile Matter	74.8 ~ 81.2	75.0 ~ 82.5	75.8 ~ 79.5
	Fixed Carbon	18.8 ~ 25.2	17.6 ~ 25.0	20.5 ~ 24.2
Higher Heating Value	BTU / lb	7641 ~ 8160	7801 ~ 8285	7851 ~ 8070
Ash composition (%w / w ash)	Na2O	0.0 ~ 0.5	0.1 ~ 4.0	0.1 ~ 0.7
	K2O	15.2 ~ 43.1	4.4 ~ 29.0	1.6 ~ 15.7
	SiO2	12.1 ~ 55.8	25.4 ~ 78.4	55.6 ~ 82.9
	CaO	8.2 ~ 27.0	5.8 ~ 25.0	8.0 ~ 20.7
	P2O5	3.5 ~ 17.1	1.4 ~ 11.0	0.9 ~ 5.4
	Al2O3	0.1 ~ 1.8	0.1 ~ 1.0	0.3 ~ 2.7
	Fe2O3	0.2 ~ 0.7	0.1 ~ 0.5	0.2 ~ 1.3
	MgO	6.8 ~ 25.6	3.7 ~ 18.8	1.7 ~ 9.0
	MnO	0.1 ~ 0.4	0.1 ~ 1.0	0.1 ~ 0.4
	TiO2	0.0 ~ 0.2	0.0 ~ 0.1	0.0 ~ 0.2
	SO3	2.3 ~ 13.1	1.5 ~ 5.4	1.3 ~ 3.5

Table 8. Thermochemical analysis of three major feedstocks (sorghum, switchgrass, and miscanthus)

TASK D2: FEEDSTOCK PREPROCESSING

Pelletization tests with switchgrass and sorghum samples have been executed by the wood pelletizing specialist Amandus Kahl to determine the appropriate pelletization equipment and process parameters for a large scale pellet plant (> 40,000 t/a). Three varieties of switchgrass (*Panicum virgatum* EG 2101, EG 1101 and EG 1102) and one sorghum hybrid (*Sorghum bicolor,* ES5200) were examined.

The tests were executed in two steps. First, each material was ground separately on a 6 mm and on a 12 mm pan grinder mill (780 mm, thickness 58 mm of die). Then, each ground material was pelletized on a 6 mm and 8 mm pellet press (390 mm, thickness 60 mm of die) (Figure 2).

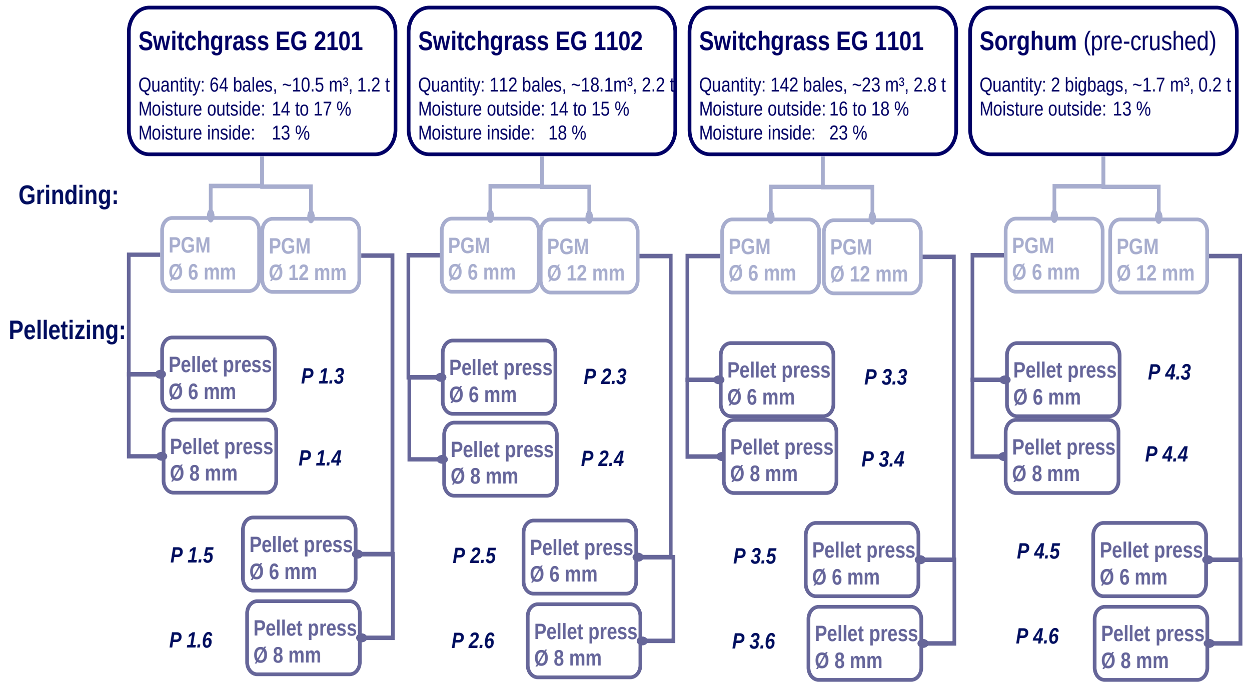


Figure 2. Test procedure of switchgrass and sorghum pelletization tests

Throughout the test series, the following parameters were documented:

- Moisture of material before and after process step
- Temperature of material before and after process step
- Bulk density before and after process step
- Hydraulic pressure
- Electricity consumption
- Throughput
- Hardness, fines and ash content of final product

Regarding the pre-crushing step, all materials could be easily defibered by using the pan grinder mill (sorghum material has already been delivered pre-crushed). The initial moisture variations of the feedstock, which could pose an issue for the stability of the final pellets, were minimized by means of the grinding process. The pan grinder worked at 20-25% of its full capacity due to the poor handling and transportation properties of the material and to the constraints in the equipment feeding area. Feedstock stalks piled up above the hydraulic nut if too much product was supplied hence limiting the material feeding rate. Thus, the pan grinder mill of a specialized pellet plant would need to be of bigger dimensions and equipped with a special feed in system.

Figure 3. Switchgrass bales being loaded onto a conveyor belt and milled switchgrass after grinding

Stable pellets were produced by using a die with 6 mm holes. The application of an additional binder was not necessary. However, a small amount of water was added via a two-component nozzle. When applying the 8 mm die, the process became unstable as soon as the water content within the raw material varied (started at a moisture difference of only 1%). The pellets' surface showed a slightly cracked surface.

Figure 4. Pellet mill test stand at Amandus Kahl and pelletized switchgrass using a 6mm die

Regarding the pelletization process as well as the pellet characteristics, the type of the pan grinder mill (differing in size of the holes and hence different size of particles) does not have a significant impact. This might become relevant, if a customer is grinding the pellets and holds special requirements concerning the particle size. In this case, the precrushing step might be adapted to the customer's needs. The pellets with the highest abrasion hardness and thus with the lowest fines share were produced on a 390*60*6 mm (diameter*thickness*size of holes) die. When applying the 390*72*8 mm dice, a generally higher demand of additional water and increased energy consumption was documented. The pellets were less stable with a higher share of fines. The increased energy input caused the moisture inside the pellet to vaporize within the die. After compression, the steam releases from the pellets, leaving small cracks in the surface and destabilizing the pellet.

The characteristics of the switchgrass pellets produced on the 6 mm dice have been compared to eight different pellet standards from Europe and the USA. The data shown in Figure 2 represents a range of six measurements of EG 2101, EG 1102 and EG 1101. Due to relatively higher nitrogen and sulfur content, switchgrass samples were not comparable to European pellet standards designed for woody biomass. The high ash content makes the pellets unsuitable for domestic heating application according to European as well as U.S. standards. Although the European industrial standard is not being met, industrial customers do not necessarily insist on compliance. Supply agreements could be set up individually regarding the customer's specific requirements and thresholds for each process. As the fines content is too high, switchgrass pellets fail to meet the American PFI Utility standard as well. However, an additional sieving step after pelletizing might solve this issue relatively easily.

As some chemical characteristics of the pelletized switchgrass were not fully investigated, especially chlorine and ash melting point, further examinations will be necessary. According to analyses of these feedstocks prior to pelletization, the chlorine content of other switchgrass varieties exceeds 0.17 % of dry matter and thus could cause potential issues if we compare currently established standards for woody biomass. It yet has to be examined whether the removal (i.e. through water extractions / leaching) would be necessary and/or economically feasible.

Torrefaction, milling and fluidization tests

The wood and switchgrass samples were torrefied by the French torrefaction company Thermya. Three different torrefaction temperatures for both wood and switchgrass were used and the respective milling properties were tested. These samples were then transported to the CHOREN laboratory in Freiberg in order to assess the fluidization properties of different particle sizes produced at different torrefaction temperatures.

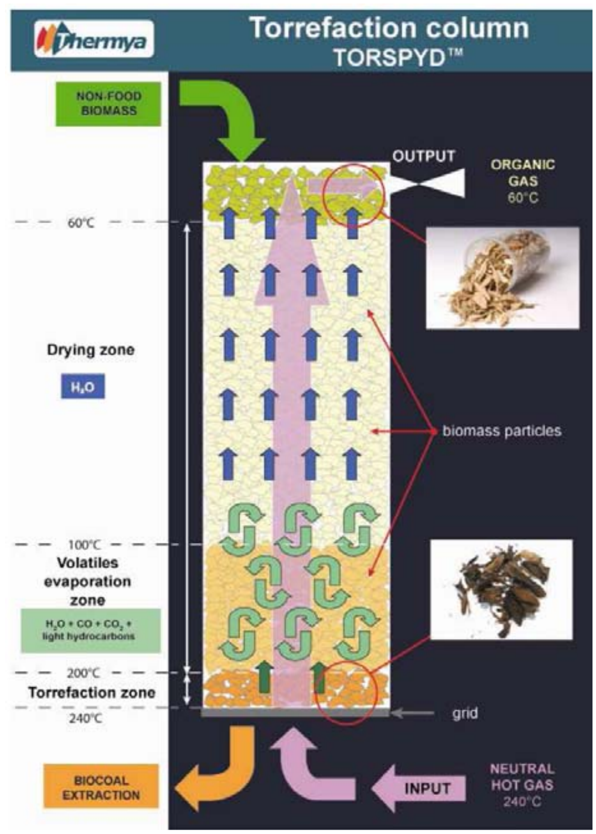


Figure 5. Description of Torspyd process

There are different technological approaches towards the torrefaction of biomass. Torrefaction can be achieved using - among others - heated screw drives, rotary kilns, fluidized bed reactors, fixed bed reactors or moving bed reactors.

CHOREN chose for its torrefaction experiments a moving bed reactor designed by the French engineering company Thermya. The Torspyd™ process (see Figure 5) is currently being commercialized in Europe and North America and allows for the production of a homogenous product quality. It can process both herbaceous and woody biomass feedstocks with different particle size distributions.

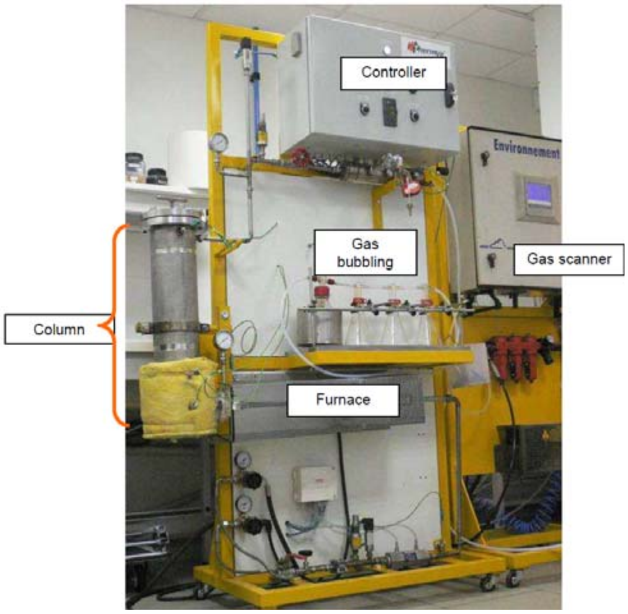


Figure 6. Monocycle laboratory torrefaction pilot

Figure 7. Wood samples before and after torrefaction

As a benchmark for the torrefaction results of the switchgrass samples, woody biomass has been torrefied and tested under the same parameters.

In a first step, woody biomass in the form of maritime pine was torrefied at three different torrefaction temperatures using Thermya's monocycle laboratory pilot (Figure 6 and Figure 7). The same was done with the switchgrass samples and the following results were achieved (Figure 8 and Table 9):

sample	calorific value / dry basis (J/kg)	torrefaction temperature (C°)	density (kg/m³)	mass yield / dry basis (%)	energy yield / dry basis (%)
initial wood sample	19.500	-	200	100,0	100,0
MPL Tor 240	20.500	240	175	85,6	90,0
MPL Tor 260	22.491	260	165	71,9	83,0
MPL Tor 280	24.448	280	155	54,6	68,5
initial switchgrass sample	19.500	-	200	100,0	100,0
SWG Tor 240	20.500	240	175	85,6	90,0
SWG Tor 260	22.491	260	165	71,9	83,0
SWG Tor 280	24.448	280	155	54,6	68,5

sample	volatile matter / dry basis	ash content / dry basis	fixed carbon / dry basis
initial wood sample	77,2	0,1	22,6
MPL Tor 240	71,8	0,2	28,0
MPL Tor 260	67,0	0,2	32,7
MPL Tor 280	55,6	0,3	44,1
initial switchgrass sample	77,2	0,1	22,6
SWG Tor 240	71,8	0,2	28,0
SWG Tor 260	67,0	0,2	32,7
SWG Tor 280	55,6	0,3	44,1

Table 9. Results torrefaction test; woody biomass versus switchgrass

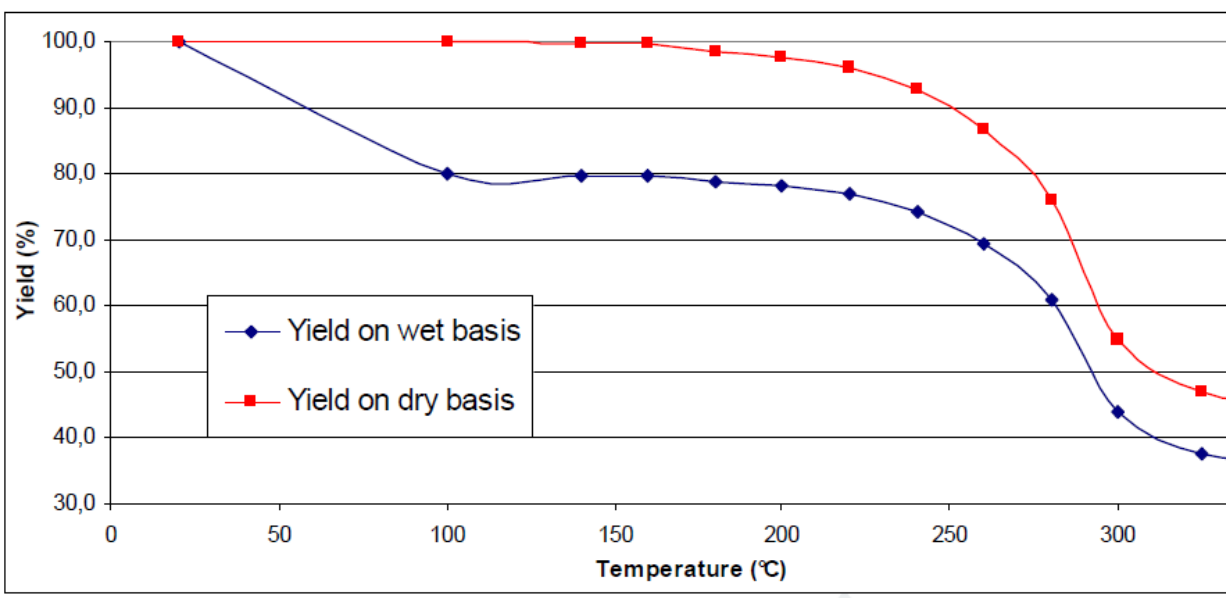
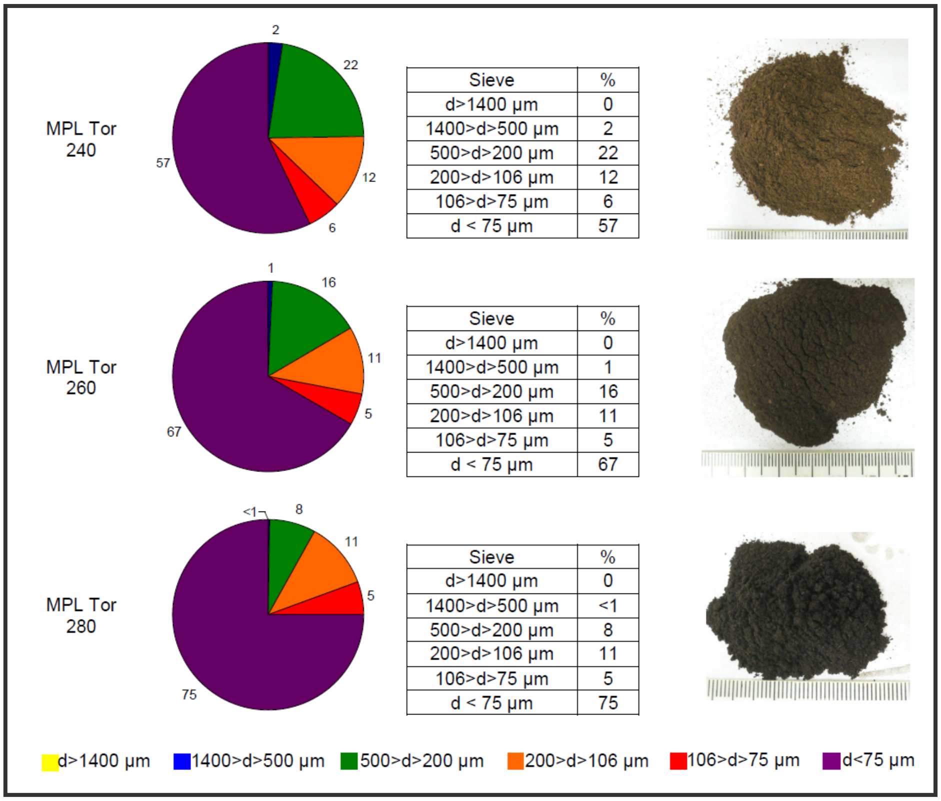


Figure 8. Evolution of mass yield based on torrefaction temperature

After the production of the different torrefaction samples, grinding tests were done in order to assess the grindability of materials produced at different torrefaction temperatures.



Sieve	%
d>1400 µm	0
1400>d>500 µm	2
500>d>200 µm	22
200>d>106 µm	12
106>d>75 µm	6
d < 75 µm	57

Sieve	%
d>1400 µm	0
1400>d>500 µm	1
500>d>200 µm	16
200>d>106 µm	11
106>d>75 µm	5
d < 75 µm	67

Sieve	%
d>1400 µm	0
1400>d>500 µm	<1
500>d>200 µm	8
200>d>106 µm	11
106>d>75 µm	5
d < 75 µm	75

Figure 9. Grinding test results

Figure 10. Fluidization test cylinder

Each torrefied product was ground for 10 minutes using a mechanical mortar grinder with the pressure vernier fixed at zero. Once ground, the torrefied product was sieved on a stack of vibrant sieves.

The results are shown in Figure 9 and clearly indicate that already mild torrefaction can lead to very low particle sizes of below 200 µm for more than 75% of the ground material. Higher torrefaction grades can increase that share to 90%.

The main goal of the experimental fluidization tests was to characterize the fluidization behavior and the optimum grade of torrefaction of the tested materials. Within the process steps from torrefaction to entrained flow gasification, the material needs to be ground and transported into the gasifier. Grinding processes need a relatively high amount of energy. The higher the grade of torrefaction the less energy is needed to achieve a certain particle size distribution. At the same time a higher grade of torrefaction reduces the energy efficiency of the torrefaction process itself - ultimately raising the feedstock costs. Therefore the optimum grade of torrefaction had to be identified that would allow for a suitable fluidization behaviour of the torrefied and grounded material at the lowest possible grade of torrefaction.

The specific energy consumption for the grinding process can be measured via the Hardgrove Test grinding test.

In order to measure the fluidization properties that are needed for a pneumatic transport system like dense phase conveying that is used for the transportation of pulverized materials into pressurized reactor vessels, a fluidized bed apparatus is used.

Figure 11. Flow rate measurement

Different types (proveniences) of biomass as well as different torrefaction qualities were analyzed and the experimental tests were structured in three parts:

- Characterize material parameters
- Characterize grindability parameters
- Characterize fluidization parameters

For characterization of material parameters, the following parameters were measured:

- Moisture content
- Lower heat value
- Ash content
- Bulk and raw density at different comminution steps
- Granulometric properties at different comminution steps

To characterize the grindability of the different types of torrefaction material, the Hardgrove Grindability Test is used, which is a standardized ASTM test (ASTM D 409-71), developed to characterize the grindability of coal.

The influence of initial bed height and material fines of torrefied material has been analyzed and the effect of the initial bed height is measured at the Levels 200, 250 and 300mm. To characterize the effect of material fines, the three comminution steps <500, < 250 and < 125µm are used. The material was put into a cylindrical glass vessel (see Figure 10).

Each sample was ground in four steps using a Retsch SM 2000 or a Retsch ZM 2000 mill. After the first grinding step at 1mm, two samples of each material were taken for grindability analysis. By means of a second grinding step the material is ground down to < 500µm. Two material samples were produced by statistic methods to measure the particle size distribution by aero stream sieve (Alpine Air Screen) and laser granulometry (Sympatec). Afterwards the material was filled into to the process volume up to a defined initial bed high. The fluidization tests were done by variation of the upstream velocity of the fluidization gas. At defined gas velocities the height and the pressure loss across the fluidization bed were measured. The fluidization tests were repeated three times to increase the confidence level. Three different initial bed heights were tested for each material. The test procedure was repeated for the 3rd and 4th grinding step at 250µm and 125µm.

For each sample, moisture content, heat value and ash content were measured. By the help of a Zeisel test machine the Hardgrove grindability index was measured.

dswirl = 300mm
ρbulk = 314 [kg/m³] at smaller 500mm
g 9,81 [m/s²]

gross density [g/cm³]					
weight [g]					
date/time		30.06.2011; 15:20			
sample number		III / 2.1			
material		STR 2 < 125 µm			
Volume stream	**uFl**	**p1**	**p2**	**H**	**Remarks**
[l/h]	**[cm/s]**	**[mmWS]**	**[mmWS]**	**mm**	
0	0,00	8	-4	260	no movement
100	0,51	-4,5	9,5	260	little volcano
200	1,02	-15	20	360	little volcano
300	1,53	-16	21	380	smooth surface
400	2,04	-16,5	21,5	380	smooth surface
500	2,55	-17	22	410	smooth surface
600	3,06	-17,5	22,5	440	little gas bubbles
800	4,07	-19	24	480	homogeneous, some gas bubbles
1000	5,09	-20	25	510	homogeneous, some gas bubbles
1200	6,11	-21,5	26,5	540	medium volcanos, big gas bubbles
1500	7,64	-24	29	590	medium volcanos, big gas bubbles
2000	10,19	-25	30	600	medium volcanos, big gas bubbles, shortly before pneumatic transportation
loss in g					

Table 10. Example test result of fluidization test

Both wood and switchgrass showed sufficiently good milling and fluidization properties for dense flow transportation into a fluidized bed gasifier at a torrefaction temperature of around 270 degrees Celsius and a particle size between 250 and 500 µm.

These are very promising results as they document the potential of the torrefaction preconditioning technology for use of switchgrass in both direct biomass gasification in large scale entrained flow gasifiers and biomass co-firing in large scale coal power plants.

TASK D3: THERMOCHEMICAL PROCESS SIMULATION (CARBO-V® PROCESS MODELING)

CHOREN applies the steady state simulation tool PRO/II from Invensys System Inc. for the simulation of the Carbo-V gasification process, the downstream syngas conditioning and the fuel synthesis processes. PRO/II was originally developed by Invensys for petrochemical processes. Utilizing the PRO/II framework as a basis, CHOREN had early on developed proprietary customized models for its gasification process. These tailored models were used for the current grant work.

CHOREN calculated six cases (for the gasification and downstream units) for three different switchgrass samples and for three different willow specifications. The specifications were delivered within the Ceres project:

1. Switchgrass, case 1: SGS IF sample no. 100306137 (Panicum virgatum 7013872-M03)
2. Switchgrass, case 2: SGS IF sample no. 100306138 (Panicum virgatum 7013874-M04)
3. Switchgrass, case 3: SGS IF sample no. 100306139 (Panicum virgatum 7013877-M02)
4. Willow, case 1: sample no. 8000073-M01
5. Willow, case 2: sample no. 8000078-M01
6. Willow, case 3: sample no. 8000082-M01

For willow, the moisture content was assumed to be 15 wt%.

The calculation outcomes have been summarized in Table 11.

		willow case 1	willow case 2	willow case 3	switchgrass case 1	switchgrass case 2	switchgrass case 3
Sample no.		8000073-M01	8000078-M01	8000082-M01	100306137	100306138	100306139
Biomass wet input	kg/h	10571	10571	10571	10571	10571	10571
Biomass C	kg/kg	41.52%	41.45%	41.08%	43.53%	43.94%	43.72%
Biomass H	kg/kg	5.05%	4.98%	5.06%	5.24%	5.25%	5.23%
Biomass O	kg/kg	37.15%	37.07%	37.57%	37.42%	37.66%	37.16%
Biomass N	kg/kg	0.20%	0.26%	0.22%	0.64%	0.57%	0.71%
Biomass S	kg/kg	0.02%	0.02%	0.02%	0.04%	0.05%	0.04%
Biomass Cl	kg/kg	0.00%	0.00%	0.00%	0.36%	0.33%	0.30%
Biomass F	kg/kg	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
Ash	kg/kg	1.05%	1.22%	1.05%	3.26%	2.81%	3.54%
Moisture	kg/kg	**15.00%**	**15.00%**	**15.00%**	**9.50%**	**9.40%**	**9.30%**
Biomass dry	kg/h	8985	8985	8985	9567	9577	9588
Rawgas ($CO+H_2$) / Biomass dry	Nm³/kg	**1.208**	**1.201**	**1.190**	**1.239**	**1.249**	**1.245**
LHV efficiency (cold gas efficiency)	%	**77.32%**	**77.26%**	**77.08%**	**79.48%**	**79.63%**	**79.55%**
Remark: LHV efficiency =[LHV output rawgas dustfree (mainly $CO + H_2$)] / [LHV input (biomass+burner feed gases, i.e. mainly biomass)]							

Table 11. Results of gasification calculation

The key conclusions from the computer simulation are:

The favorable overall cold gas efficiency[1] of about approximately 80% is a result of the chemical quench in CHOREN's proprietary Carbo-V® process. Chemical quench in this regard means the endothermic conversion of carbon into hydrogen and carbon monoxide in the third stage of the Carbo-V® process by utilizing the sensible heat of the hot synthesis gas exiting the second stage of the Carbo-V® reactor.

Average cold gas efficiency for switchgrass is 3-4% higher than for willow, due to the lower moisture content of switchgrass. However, lower moisture content usually implies higher costs

[1] The cold gas efficiency is defined as the ratio between the lower heating value of the raw synthesis gas outlet stream (CO, H_2, CH_4) and the total energy input (biomass + natural gas for support burners) as lower heating value.

for drying the biomass. Drying requirements for switchgrass are considerably lower or negligible and thus in this case a yield advantage is achieved at no additional cost.

The PRO/II simulation proves the theoretical applicability of the Carbo-V® process on switchgrass and willow. However, the commercial application of these feedstocks in the Carbo-V® gasification process still needs to be proven.

TASK D4: DATA ANALYSIS AND REPORT (ECONOMIC COMPARISON SWITCHGRASS VS. WILLOW)

An evaluation was done to identify the economic impact of using switchgrass as a feedstock for syngas production via CHOREN's Carbo-V technology versus using another type of dedicated energy wood crop such as willow wood chips.

Both calculations were done under the assumption that both switchgrass or willow would be used as a 100 percent feedstock. Switchgrass costs were estimated on the basis of $50-70/odmt (baled) with additional costs for pelletization of $20-40/odmt resulting in an overall estimated price range of $70-110/odmt delivered to the gate of the biorefinery (source Ceres) at about 10% moisture content.

The price range for dedicated and pre-dried (15% moisture content) willow wood chips were calculated between $60-100/odmt and mirror the price range of pulp wood chips in the South Eastern U.S.

Parameter	Units	Willow at $60/odmt	Switchgrass at $70/odmt
Moisture content	%wt	15	9.4
Bulk density	kg/m^3	200	600
Biomass dry per Nm^3 (raw) syngas ($CO+H_2$)	Metric ton/Thousand Nm^3	0.834	0.804
Raw syngas cost[2]	$/Thousand Nm^3	50.02	56.25

Table 12. Comparison of syngas cost for switchgrass and willow

[2] It is assumed that downstream operations and Syngas treatment costs are equal for both feedstocks

As Table 12 shows, the advantage of the better cold gas efficiency achieved with switchgrass is outweighed by the cost for pelletizing the feedstock, resulting in about 10% higher syngas cost. The table also shows that the pelletized switchgrass material exhibits a higher bulk density than willow, which could be an advantage by requiring less capital expenditure for biomass handling equipment, such as conveyors, silos, etc. However, it is questionable whether the savings in capital investment would be preferable to a lower variable feedstock cost. Such an assessment was not part of the scope of this study.

Nevertheless, switchgrass has the advantage of being a faster rotation crop than woody biomass species, and it can be established at minimal costs, which allows for a much faster growth in overall volumes produced in a certain region while still allowing the producing farming community to maintain full flexibility on their land use pattern. It is also likely that improvements in switchgrass yields will likely bring the feedstock costs down in the near- to mid-term, whereas woodchips may increase in price due to increased demand.

From a capital expenditure perspective, a bio-refinery handling multiple types of feedstock will incur a higher investment cost than one with a dedicated feedstock. On the other hand, to ensure optimal availability, having more than one feedstock supply source can be a great advantage in respect to supply risk mitigation.

CONCLUSION AND OUTLOOK

Tasks C and D showed that woody biomass such as willow wood chips from short rotation plantations as well as high yielding energy grasses such as switchgrass can be potentially used for the production of green syngas at an industrial scale.

The characterization of the different plant varieties (Task B and Task D.1) did not show significant differences in those specifications relevant for biomass gasification that could merely be attributed to the genetic material of the plant rather than to the different soils they were growing on. Environment appears to have a more significant impact on composition and performance in a gasification process than genetics. Generally, the ash content in switchgrass (and most grasses) was observed to be higher than in willow (and most trees), but low ash switchgrass samples were identified that were comparable to high ash willow samples. Ash composition, ash melting behavior and total ash content differed only within a narrow range. The low moisture content of switchgrass was a significant benefit of the herbaceous feedstocks over the woody species.

For a commercial biorefinery, the most important issues are the economic aspects of the different plant materials. Costs per Giga Joule harvested are primarily linked to the difference in total biomass yield per growing season and the water content of the plant during harvesting.

The pelletization tests conducted under Task D.2 for switchgrass showed very promising results. The feedstock densification and improved handling characteristics of pelletized materials could make this approach with herbaceous feedstocks desirable.

Also included in task D.2, the torrefaction and fluidization tests on both woody and herbaceous biomass clearly indicated that adequately pretreated biomass can directly be used as a feedstock for pneumatic high pressure transportation and opens the downstream use of conversion technologies formerly restricted to fossil coal such as powder burner and entrained flow gasifiers. Overall, the conducted tests have shown that there is no relevant difference between torrefied woody biomass and torrefied switchgrass, and that both should be suitable for use in commercial coal-fired gasifiers

The Carbo-V® process simulation (Task D.3) showed that pelletized switchgrass can achieve a better theoretical yield (4%) than willow wood chips, mostly due to its relative low moisture and moderate ash content.

Task D.4 highlighted the economic impact of both switchgrass and willow feedstocks on the cost of raw Syngas production. The advantage of the better cold gas efficiency achieved with switchgrass is outweighed by the cost for pelletizing the feedstock, resulting in about 10% higher raw syngas cost. The data show that the pelletized switchgrass material exhibits a higher bulk density than willow, which may result in less capital expenditure for biomass handling equipment.

The results in this study are primarily based on laboratory scale tests and theoretical calculations. Verification at a demonstration or commercial scale plant is required in order to substantiate the findings within this report.