DEPARTMENT OF CHEMISTRY

DIVISION OF ORGANIC CHEMISTRY
HEAD OF DEPARTMENT: UNIV. PROF. DR. PAUL KOSMA

SUPERVISORS: AO. UNIV. PROF. DR. ANTJE POTTHAST
UNIV. PROF. DR. THOMAS ROSENAU

GREEN REFINERY - IONIC LIQUIDS AS NOVEL MEDIA FOR BIOMASS PROCESSING

DISSERTATION FOR OBTAINING THE DOCTORAL DEGREE
UNIVERSITY OF NATURAL RESOURCES AND LIFE SCIENCES, VIENNA

SUBMITTED BY
MAG. MICHAEL SCHREMS, MBA

VIENNA, JULY 2011

To my parents, Regina and Helmut

Here I want to thank my parents for their financial and emotional support during all the years of study. On the long way of becoming a self-confident, qualified scientist they strengthened me when doubts got out of hand and paved the way as good as they could by removing all obstacles outside the very individual world of science. Their commitment and patronage allowed me to achieve all my goals rather quickly making them a legitimate part of this success. With parents like they are one can master even the biggest challenges in career and life.

FOR ANGELIKA

HERE I WANT TO THANK ANGELIKA, MY WIFE, SOUL MATE, BEST FRIEND, LONGTIME LAB-PARTNER AND COLLEAGUE FOR ALWAYS BEING ON MY SIDE, FOR BETTER OR FOR WORSE. WITHOUT HER I WOULDN'T BE WHERE I AM TODAY AN MORE IMPORTANT WHO I AM TODAY. HER STRONG BELIEF IN ME, HER UNPARALLELED SUPPORT IN ENDLESS DISCUSSIONS AND HER LOVE MADE IT POSSIBLE TO MANAGE ALL TASKS AND STAND ALL SETBACKS AND ALL THE FRUSTRATION ON THE WAY TO GRADUATION. THANK YOU FOR STEPPING INTO MY LIFE AND BRIGHTEN EVERY DAY WITH YOUR SMILE. WITH YOU AS PARTNER: *IMPOSSIBLE IS NOTHING!*

"WE CHEMISTS ARE PROUD
OF OUR ABILITY TO CREATE
HIGH VALUES FROM ALMOST
NOTHING ON THE BASIS OF
ACCUMULATED SCIENTIFIC
KNOWLEDGE"

(RYOJI NOYORI)

ACKNOWLEDGEMENTS

"In the long history of humankind (and animal kind, too) those who learned to collaborate and improvise most effectively have prevailed" Charles darwin once said.

A work like the presented one can't be done without the help and support of others who are often forgotten when it comes to an end. Of course many more contributed with their knowledge, their time, their patience and their openness who are not explicitly mentioned but nevertheless important for the completion and success of this work. In the following I want to thank all people who made it possible or simply gave me a good time over the years.

Thank you

Colleagues

Manuel Becker	For his endless cooperativeness and expertise regarding sugars, chromatography and evaluation
Markus Blaukopf	For suggestive discussions, criticism, being the master of the magnetic monster (NMR) and countless IT savior
Anna Bogolitsyna	For interesting discussions, friendliness and being a pleasant and supportive neighbor in lab and office
Gerald Ebner	For being the ideal colleague through his outstanding cooperativeness and indestructible good mood
Emmerich Haimer	For being the master of the mechanical stuff, his instant solutions and knowledge about $scCO_2$
Ute Henniges	For her support with all tasks related to GPC and Taking care that everything keeps running and its order
Martina Opietnik	For her advices, discussions, support, time and for her distinct sense of humor

GEORG POUR	FOR BEING COLLEAGUE AND FRIEND BREAKING UP DAILY ROUTINE WITH JOKES, STORIES, GOOD MUSIC AND FUNNY VIDS
SONJA SCHIEHSER	FOR HER HELP AND PATIENCE IN PREPARING SAMPLES FOR GPC AND NUMEROUS DISCUSSIONS ABOUT ANYTHING AND EVERYTHING
CHRISTIAN STANETTY	FOR BEING FRIEND, MENTOR AND CRITICAL DISCUSSION PARTNER, HIS UPRIGHT HONESTY, FRIENDLINESS AND SARCASM

STUDENTS

SONJA BEDNARIK	FOR BEING MY FIRST STUDENT, EXCEPTIONALLY MOTIVATED, HER HONESTY, MORAL VALUES AND DEDICATION FOR SCIENCE
PHILIPP VEJDOVSZKY	FOR BEING A RELIABLE, DILIGENT STUDENT AND COWORKER, EAGER FOR KNOWLEDGE AND HIGH DEGREE OF SELF-RELIANCE

SUPERVISORS

ANTJE POTTHAST	FOR GUIDANCE ON THE WAY TO AN INDEPENDENT RESEARCHER, HER TIME, RELIABILITY, HONESTY AND DIRECTNESS
THOMAS ROSENAU	FOR BEING A GOOD MENTOR, TEACHER AND BOSS ALWAYS HAVING A SYMPATHETIC EAR, TIME AND ADMINISTRABLE ADVICES
FALK LIEBNER	FOR HIS NUMEROUS CORRECTIONS, VALUABLE INPUT, TIME, ACCURACY AND A GOOD SENSE OF HUMOR

ABSTRACT

Fading fossil resources with a simultaneously increasing demand for energy generate a strong need for new technologies based on renewable, inexhaustible resources. The development of potentially green technologies based on renewable feedstock's is one of the main challenges for mankind in the next decades and centuries underlining the social and economical importance of research conducted in this area.

In this work, several efforts have been made towards a better understanding of lignocellulose as feedstock for future technologies and its utilization in biorefinery processes. A new Organosolv-based biorefinery concept has been evaluated towards its applicability to make such concepts more economically feasible. Lignin as source for artificial humic substance to combat progressive desertification in parts of the world was considered as most promising value added product in this regard. High delignification rates of about 70% could be achieved by using supercritical carbon dioxide as a co-solvent. Aqueous ammonium hydroxide as pulping additive led to a considerable nitrogen enrichment in the lignin fraction which allows saving a significant amount of energy by avoiding the intermediate purification of the lignin prior to N-modification. A nitrogen enrichment of 4% combined with a fraction purity of 80-85% renders this product applicable for the aimed purpose of soil improvement. The effect of supercritical carbon dioxide on the delignification rate has been investigated in more detail using apocynol as a monomeric lignin model substance. This study revealed that supercritical carbon dioxide accelerates the degradation of the model substance and significantly lowers the activation energy for this reaction hence supporting its use as co-solvent during pulping when aiming for maximal lignin output.

Ionic liquids were investigated as powerful solvent and reaction media for cellulose in its pure form and in its naturally surrounding matrix including hemicelluloses and lignin. It was shown that these solvents are not entirely inert and thus have to be selected carefully. Investigation of the dissolution mechanism of lignocellulose in ionic liquids revealed an ongoing degradation of the solute in dependence of temperature and solvent purity. Finally, ionic liquids were shown capable to significantly reduce the energy demand of mechanical crushing steps in wood-based technologies as a consequence of their lubricating nature.

ZUSAMMENFASSUNG

ZU NEIGE GEHENDE FOSSILE ENERGIETRÄGER UND EIN GLEICHZEITIG STEIGENDER ENERGIEBEDARF ERZEUGEN EIN STARKES BEDÜRFNIS FÜR NEUE, AUF NACHWACHSENDEN, UNERSCHÖPFLICHEN ROHSTOFFEN BASIERENDE TECHNOLOGIEN. DIE ENTWICKLUNG VON GRÜNEN TECHNOLOGIEN AUFBAUEND AUF ERNEUERBAREN ROHSTOFFEN STELLT EINE DER GRÖSSTEN HERAUSFORDERUNGEN DER MENSCHHEIT IN DEN NÄCHSTEN JAHRZEHNTEN UND JAHRHUNDERTEN DAR UND DAHER VON HOHER SOZIALER UND ÖKONOMISCHER BEDEUTUNG.

IN DIESER ARBEIT SIND VERSCHIEDENE ANSTRENGUNGEN UNTERNOMMEN WORDEN, UM EIN BESSERES VERSTÄNDNIS DIESES ROHSTOFFS ZUKÜNFTIGER TECHNOLOGIEN ZU ERLANGEN. DABEI IST EIN NEUES ORGANOSOLV-BASIERENDES BIORAFFINERIEKONZEPT HINSICHTLICH SEINER EIGNUNG, SOLCHE KONZEPTE WIRTSCHAFTLICHER ZU MACHEN, UNTERSUCHT WORDEN. LIGNIN ALS AUSGANGSSTOFF FÜR KÜNSTLICHE HUMUSERSATZSTOFFE ALS ANTWORT AUF FORTSCHREITENDE WÜSTENBILDUNG IN TEILEN DER ERDE ERSCHIEN DABEI ALS DAS VIELVERSPRECHENDSTE MEHRWERTPRODUKT. HOHE DELIGNIFIZIERUNGSRATEN VON CA. 70% KONNTEN DURCH EINSATZ VON SUPERKRITISCHEM CO_2 ERREICHT WERDEN. DER EINSATZ VON WÄSSRIGEM AMMONIUMHYDROXID ALS PULPINGZUSATZSTOFF FÜHRTE ZU EINER BEACHTLICHEN STICKSTOFFANREICHERUNG IN DER LIGNINFRACTION, WAS ENERGETISCHE EINSPARUNGEN ERMÖGLICH, DA DIE INTERMEDIÄRE REINUNG VOR DER N-MODIFIKATION ENTFÄLLT. EINE STICKSTOFFANREICHERUNG VON 4% BEI EINER FRAKTIONSREINHEIT VON 80-85% IST HINREICHEND FÜR DIE BEABSICHTIGTE VERWENDUNG ALS BODENVERBESSERER. DER EFFEKT VON SUPERKRITISCHEM CO_2 AUF DIE DELIGNIFIZIERUNGSRATE WURDE IM RAHMEN EINER MODELLSUBSTANZSTUDIE UNTER VERWENDUNG VON APOCYNOL, EINER MONOMEREN LIGNINMODELLSUBSTANZ, GENAUER UNTERSUCHT. DIESE STUDIE HAT GEZEIGT, DASS SUPERKRITISCHES CO_2 DEN ABBAU DER MODELLSUBSTANZ BESCHLEUNIGT UND DIE AKTIVIERUNGSENERGIE DIESER REAKTION DEUTLICH HERABSETZT, WAS DESSEN EINSATZ ALS LÖSUNGSMITTEL ZUR ERREICHUNG HOHER DELIGNIFIZIERUNGSRATEN RECHTFERTIGT.

IONISCHE FLÜSSIGKEITEN WURDEN IN DIESEM RAHMEN WEGEN IHRER HOHEN LÖSEKRAFT, SOWOHL FÜR CELLULOSE IN REINFORM ALS AUCH IM NATÜRLICHEN VERBUND MIT HEMICELLULOSEN UND LIGNIN, UNTERSUCHT. ES KONNTE GEZEIGT WERDEN, DASS DIESE LÖSUNGSMITTELKLASSE NICHT GENERELL INERT IST UND DAHER SORGFÄLTIG AUSGEWÄHLT WERDEN MUSS. UNTERSUCHUNGEN DES LÖSEMECHANIMUS VON LIGNOCELLULOSE IN DIESEM MEDIUM ZEIGTEN EINEN STARKEN ABBAU DER CELLULOSE IN ABHÄNGIGKEIT VON TEMPERATUR UND REINHEITSGRAD. SCHLIEßLICH KONNTE NOCH GEZEIGT WERDEN, DASS IONISCHE FLÜSSIGKEITEN FÄHIG SIND, DEN ENERGIEBEDARF IN MECHANISCHEN HOLZZERKLEINERUNGSSCHRITTEN ZU REDUZIEREN.

TABLE OF CONTENTS

1. INTRODUCTION

1.1 BIOREFINERY

"…and what is a man without energy? Nothing – nothing at all." (Mark Twain)

Living in the age of the crude oil industry awakening, Famous writer Mark Twain put one of the most important challenges of the new millennium in a nutshell – our everlasting and steadily increasing need for energy.

Fading fossil resources make it even more essential to invent and establish new technologies based on renewable sources. Recent data show that fossil energy sources as oil and gas will not be available anymore by the middle of this century and also coal, the prevalent global energy source, will have to be replaced with the dawn of the next century [Shafiee and Topal 2009]. Gas hydrates as the last remaining fossil energy source show great potential as a future energy source due to global abundance and distribution [Lee and Holder 2001]. However, difficulties in recovery and the controversially discussed impact of methane as greenhouse gas potentially affecting global warming renders this energy source as a rather uncertain replacement for current energy sources [Demirbas 2010a,b]. Nuclear Energy, a non-carbon non-renewable energy source is considered to be an energy source with long-term perspectives due to tremendous ubiquitous uranium deposits but shows several drawbacks when it comes to final disposal and overall operation security. Therefore only renewable energy sources as hydropower, solar, wind, geothermal energy and conversion of biomass can satisfy our demand for energy in the future. Though most of these alternative energy sources can possibly replace oil derived energy, new sources have to be found to provide all the side products and platform chemicals recovered and made from oil. Most of the fuel consumed worldwide to operate cars, airplanes and all kind of machines is recovered from oil by distillation. Bitumen, a viscous distillation residue, is used as seal and insulation material and gives million miles of road their typical grey-black color. numerous chemicals as short aliphatic hydrocarbons and various aromatic compounds are petrochemical products. Whole industrial sectors like the plastics industry are strongly dependent on petrochemical products and couldn't be continued without oil-derived raw materials. Out of all alternative energy sources only biomass conversion has the potential to fully replace oil as source for energy and raw materials for various products of everyday's life.

1.1.1 SUBSTRATES

SUBSTRATES FOR BIOREFINERY CONCEPTS ARE MANIFOLD. BASICALLY ALL ORGANIC MATTER CAN BE UTILIZED FOR CONVERSION INTO FUEL, POWER OR CHEMICALS. AMONG THESE SOURCES, LIGNOCELLULOSIC MATERIALS LIKE WOOD OR ANNUAL PLANTS SHOW THE GREATEST POTENTIAL IN SUPPLYING THE WORLD WITH ENERGY AND AN INCREDIBLE AMOUNT OF RAW MATERIALS FOR VARIOUS INDUSTRIAL APPLICATIONS. LIGNOCELLULOSIC FEEDSTOCK'S ARE INEXHAUSTIBLE, CHEAP SOURCES IN GLOBAL ABUNDANCE AVAILABLE FOR ALMOST EVERY NATION WITH NO NEED FOR LONG ROUTES OF TRANSPORTATION. THE POSSIBILITY TO PROCESS CROP RESIDUES AND OTHER WASTES PROVIDE CONDITIONS FOR SUSTAINABLE ECONOMIZING AND COULD PAVE THE WAY TO A POTENTIALLY GREENER WORLD. ITS HIGH COMPLEXITY IS, BESIDE GREAT OPPORTUNITIES, ALSO THE MAJOR DRAWBACK OF THESE FEEDSTOCK'S REQUIRING NEW TECHNOLOGIES WHICH ARE NOT AVAILABLE YET. LIGNOCELLULOSIC BIOMASS IS A NATURAL PRODUCT GENERATED BY CONVERTING ATMOSPHERIC CARBON DIOXIDE AND WATER INTO SUGARS AND SUBSEQUENT SYNTHESIS OF MORE COMPLEX MATERIALS THAT FORM THE RESPECTIVE ORGANISM. ALL LIGNOCELLULOSIC SOURCES CONSIST OF THREE MAIN CONSTITUENTS: CELLULOSE, HEMICELLULOSES AND LIGNIN. **TABLE 1** GIVES AN OVERVIEW ABOUT THEIR SHARE IN COMMON LIGNOCELLULOSIC FEEDSTOCK'S.

TABLE 1. LIGNOCELLULOSIC FEEDSTOCK COMPOSITIONS: COMPARING ELEMENTAL CONSTITUTION WITH PETROLEUM [CHERUBINI 2010].

	(SOFT)WOOD	SWITCH GRASS	CORN STOVER	(WHEAT) STRAW	PETROLEUM
CELLULOSE	44.5	35.4	38.1	32.6	/
HEMICELLULOSES	21.9	26.5	25.3	22.6	/
LIGNINS	27.7	18.2	20.2	16.8	/
C	50.3	46.9	46.7	43.9	83-87
H	6.0	5.5	5.5	5.3	10-14
O	42.1	42.0	38.4	38.7	0.1-1.5
N	<0.1	0.6	0.7	0.6	0.1-2
S	<0.1	0.7	0.1	0.2	0.5-6

CELLULOSE, HEMICELLULOSES AND LIGNIN ARE POLYMERS THAT CONSTITUTE THE BACKBONE OF EVERY HERBAL ORGANISM, THE CELL WALL, RESPONSIBLE FOR STABILITY AND RESISTANCE. THESE POLYMERS ARE CONNECTED IN A HIGHLY ORDERED STATE FORMING A NATURAL COMPOSITE MATERIAL INDIVIDUALLY EXPRESSED THROUGH INTERACTION OF GENETIC CODE AND ENVIRONMENTAL INFLUENCES [FAIX 2007]. EACH OF THESE POLYMERS COMPRISES SEVERAL CHARACTERISTIC FEATURES WHICH CAN BE DRAWN RESPONSIBLE FOR THEIR PLACE AND FUNCTION IN THIS COMPLEX SYSTEM. IN THE FOLLOWING, THEIR APPEARANCE AND ASSIGNMENT WILL BE DESCRIBED IN MORE DETAIL.

CELLULOSE

CELLULOSE IS THE MOST ABUNDANT ORGANIC COMPOUND ON EARTH WITH AN ANNUAL, PHOTOSYNTHETIC GENERATION OF 10^{11} TO 10^{12} TONS [KLEMM ET AL. 2002]. IT CONSISTS OF REGIO- AND ENANTIOSELECTIVELY β-1,4-GLYCOSIDIC LINKED D-GLUCOPYRANOSE UNITS (OFTEN REFERRED AS ANHYDROGLUCOSE UNITS OR AGU) FORMING A STRICTLY LINEAR, POLYDISPERSE HOMOPOLYMER WITH THE MOLECULAR FORMULA $(C_6H_{10}O_5)_n$, DETERMINED BY ANSELM PAYEN IN 1838. DUE TO A TORSION ANGLE OF 180° OF THE GLYCOSIDIC BOND CONNECTING TWO MONOMER UNITS, THE SMALLEST REPEATING UNIT COMPRISES TWO MONOMER BUILDING BLOCKS. THE HIGH STABILITY OF THIS MATERIAL ARISES FROM STRONG INTRA- AND INTER-MOLECULAR HYDROGEN BONDS WITHIN AND BETWEEN THE HOMOGLUCAN CHAINS AS SHOWN IN **FIGURE 1**.
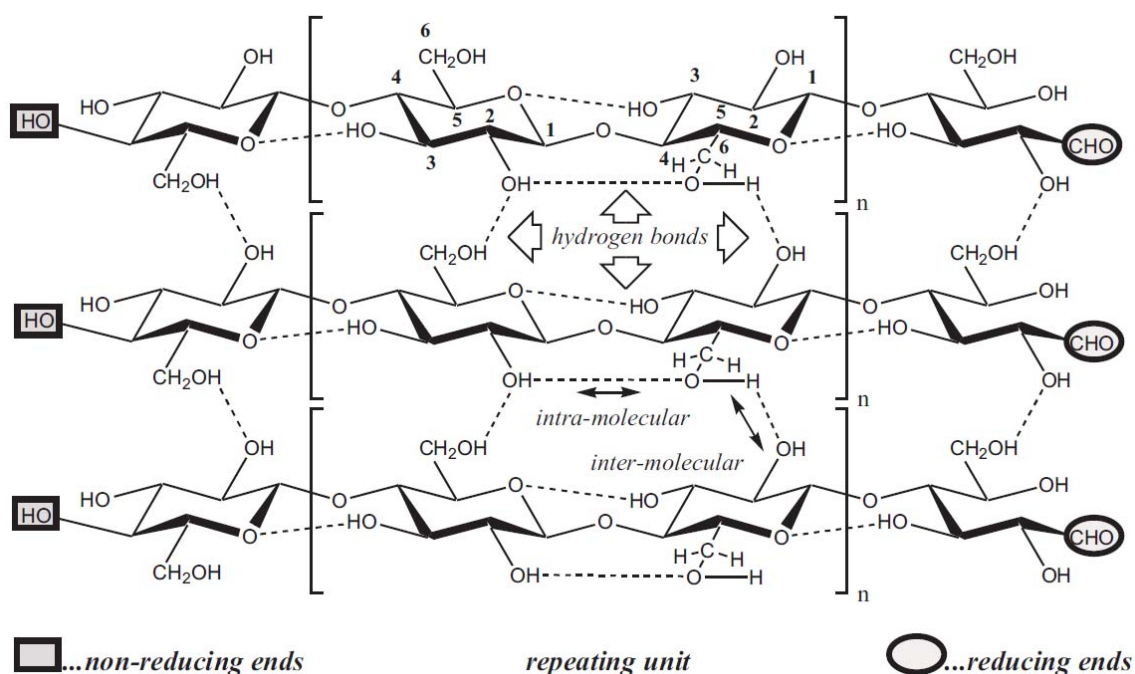

FIGURE 1. MOLECULAR STRUCTURE OF CELLULOSE I INCLUDING BOND PATTERN

THIS HIGHLY ORDERED STATE TYPICALLY LEADS TO FORMATION OF CRYSTALLITES WHICH ARE THE FUNDAMENTAL UNIT WITHIN THE SUPRAMOLECULAR STRUCTURE. AMORPHOUS APPEARANCE CAN OFTEN BE OBSERVED FOR LESS-ORDERED REGIONS OFTEN BUT NOT ONLY LOCATED ON THE OUTER SECTIONS OF THE MOLECULAR NETWORK. PLANT DERIVED CELLULOSE NATURALLY APPEARS IN ONLY ONE CRYSTAL MODIFICATION, CELLULOSE I, WITH TWO DIFFERENT CRYSTAL STRUCTURES. THE THERMODYNAMICALLY MORE STABLE CRYSTAL STRUCTURE $I_β$ IS DESCRIBED AS A MONOCLINIC UNIT CELL CONSISTING OF TWO CELLULOSE CHAINS COMPARED TO THE LESS STABLE, TRICLINIC MODIFICATION $I_α$, WHICH HAS ONLY ONE CHAIN PER UNIT CELL [ATALLA AND VANDERHART 1984; SUGIJAMA ET AL. 1991; YAMAMOTO AND HORII 1993]. CELLULOSE II CAN BE OBTAINED AFTER INDUSTRIAL PROCESSING CAUSING AND ANTIPARALLEL ALIGNMENT OF THE CELLULOSE CHAINS.

FURTHER KNOWN POLYMORPHS OF CELLULOSE E.G. CELLULOSE III, WHICH CAN BE OBTAINED BY IMMERSING CELLULOSE I OR II IN LIQUID AMMONIA FOLLOWED BY SUBSEQUENT EVAPORATION OR CELLULOSE IV, APPEAR ONLY AS A RESULT OF SPECIAL TREATMENTS. CELLULOSE IS AN ALIGNMENT OF MANY GLUCOPYRANOSE UNITS WITH CONSIDERABLE HIGH MOLECULAR WEIGHT. IN DEPENDENCE OF ORIGIN AND TREATMENT, DEGREES OF POLYMERIZATION CAN VARY BETWEEN SEVERAL HUNDRED FOR PROCESSED OR DEGRADED CELLULOSE UP TO ABOUT 20.000 FOR BACTERIAL CELLULOSE [TABUCHI ET AL. 1998]. THE HIGH STRUCTURAL STABILITY ARISES BY BUNDLING SEVERAL GLUCAN CHAINS TO FIBRILS. THESE BUNDLES OF GLUCAN CHAINS ARE DIFFERENTIATED BY THEIR DIAMETER WITH THE ELEMENTARY FIBRIL BEING SMALLEST WITH A DIAMETER ABOUT 3.5 nm [MÜHLENTHALER 1965]. THE FIRST WELL-DEFINED MORPHOLOGICAL ENTITIES ARE MICROFIBRILS WHICH CONSIST OF BUNDLES OF MANY ELEMENTARY FIBRILS HAVING DIAMETERS IN THE RANGE OF FOUR TO THIRTY-FIVE NANOMETERS [FINK ET AL. 1990]. THE LARGEST ENTITIES ARE THE MACROFIBRILS FORMED BY GROUPED MICROFIBRILS REACHING DIMENSIONS OF MICROMETERS IN DIAMETER AND LENGTH [FENGEL AND WEGENER 1989]. THESE UNITS ARE THE BUILDING BLOCKS FOUND IN THE CELL-WALL ARCHITECTURE IN LAYERS WITH DIFFERENT FIBRIL TEXTURE [KLEMM ET AL. 2002].
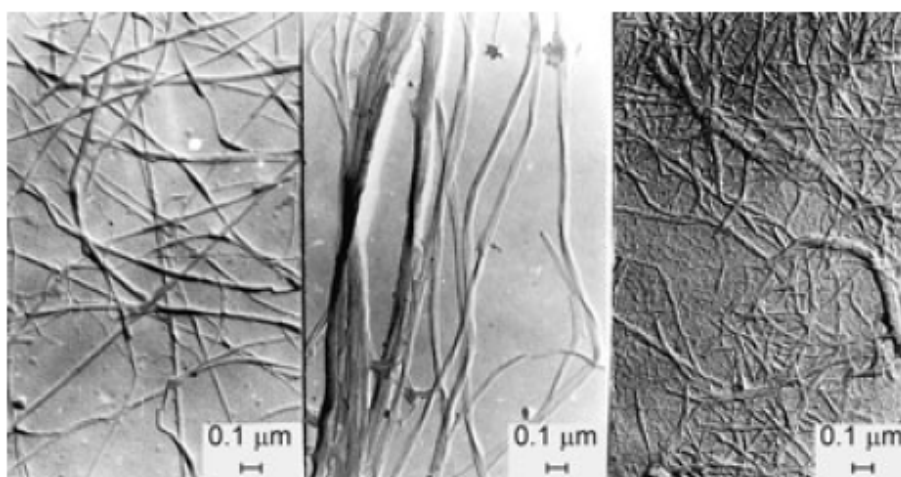

FIGURE. 2. ELECTRON MICROGRAPHS OF CELLULOSIC MICROFIBRILS OF VARYING ORIGINS. LEFT: ALGAE (VALONIA SPP.); CENTER: COTTON LINTERS; RIGHT: SPRUCE SULFITE PULPS [KLEMM ET AL. 2005].

PHYSIOLOGICAL FUNCTIONS WITHIN THE PLANT CELL-WALL ARE MANIFOLD. AS ALREADY INDICATED PREVIOUSLY, THE MAIN FUNCTION OF THE THREE MAJOR CONSTITUENTS CELLULOSE, HEMICELLULOSES AND LIGNIN IS THE FORMATION OF RIGID STRUCTURES TO PROVIDE PROTECTION OF THE PLANT ORGANISM. THESE STRUCTURES ARE ALSO IMPORTANT FOR THE PLANT MORPHOGENESIS ON THE MACROSCOPIC LEVEL. THE HYDROPHILIC CHARACTER OF CELLULOSE, ITS INSOLUBILITY IN WATER ARISING FROM THE STRONG HYDROGEN BONDS, AND PERMEABILITY FOR WATER, NUTRIENTS AND GASES PROVIDE A GOOD TRANSPORT THROUGH THE CELL. THESE CHARACTERISTICS ALSO ENABLE A PROTECTION AGAINST SWELLING WHEN WATER ENTERS THE CELL AND ARE HENCE ABSOLUTELY ESSENTIAL FOR HERBAL ORGANISM.

HEMICELLULOSE

HEMICELLULOSES ARE IN CONTRAST TO CELLULOSE NOT JUST AN ALIGNMENT OF MANY IDENTICAL UNITS. HEMICELLULOSES COMPRISE OF SEVERAL POLYSACCHARIDES WHICH CAN BE DIVIDED INTO FOUR SUPERIOR GROUPS: XYLANS (XYLOGLYCANS), MANNANS (MANNOGLYCANS), XYLOGLUCANS AND GLUCANS WITH MIXED LINKAGES. OFTEN ALSO REFERRED AS POLYOSES, THEY CONSIST OF VARIOUS MONOSUGAR UNITS INCLUDING HEXOSES (GLUCOSE, MANNOSE AND GALACTOSE), PENTOSES (XYLOSE, ARABINOSE) AND URONIC ACIDS (GLUCURONIC- AND GALACTURONIC ACID).THE STRUCTURAL PECULIARITIES OF XYLANS AND MANNANS ARE PICTURED IN **FIGURE 3**.
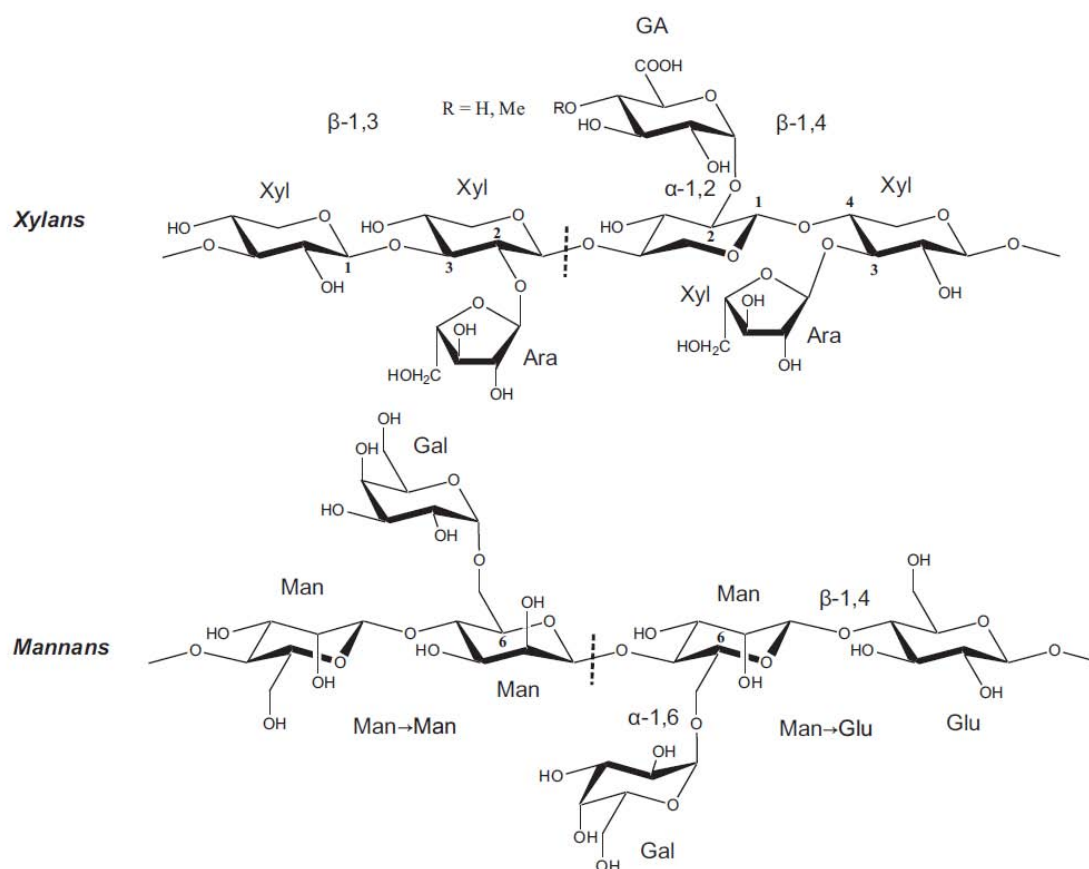

FIGURE 3. *STRUCTURAL FEATURES OF XYLANS AND MANNANS*

XYLANS ARE DIFFERENTIATED INTO HOMOXYLANS, GLUCURONOXYLANS, (ARABINO)-GLUCURONO- OR (GLUCURONO)-ARABINOXYLANS AND ARABINOXYLANS. HOMOXYLANS ARE UNBRANCHED POLYSACCHARIDES CONSISTING OF D-XYLOPYRANOSYL UNITS CONNECTED VIA β-GLYCOSIDIC BONDS 1,4; 1,3 OR MIXTURES THEREOF. GLUCURONOXYLANS ARE THE MOST ABUNDANT HEMICELLULOSES BRANCHED AT POSITION 2 WITH α-D-GLUCURONIC ACID (GA) AND/OR ITS 4-*O*-METHYL DERIVATIVE WITH AN AVERAGE SUBSTITUTION RATIO OF 1:10 [EBRINGEROVA 2006]. ARABINO-GLUCURONOXYLANS ARE ADDITIONALLY MODIFIED XYLAN CHAINS SUBSTITUTED WITH L-ARABINOSE AT POSITION 3. ARABINOXYLANS DO NOT CARRY α-D-GLUCURONIC ACID RESIDUES BUT ARE BRANCHED AT POSITION 2 AND 3 WITH L-ARABINOSE IN AN ARA:XYL RATIO OF 1:3-5.

MANNANS BASICALLY APPEAR IN TWO FORMS: AS GALACTOMANNANS AND GLUCOMANNANS. GALACTOMANNAN IS A HOMOPOLYMER CONSISTING OF β-1,4 LINKED MANNOPYRANOSYL UNITS OCCASIONALLY BRANCHED AT POSITION 6 WITH α-GALACTOSE UNITS. GLUCOMANNANS OR GALACTO-GLUCOMANNANS HAVE A HETEROGENEOUS POLYMER BACKBONE CONSISTING OF ALTERNATING β-D-MANNOPYRANOSYL AND β-D-GLUCOPYRANOSYL UNITS BRANCHED ALSO AT POSITION 6 WITH α-GALACTOSE UNITS. FURTHER HEMICELLULOSES ARE XYLOGLUCANS WITH A CELLULOSIC BACKBONE BRANCHED WITH α-D-XYLOPYRANOSYL UNITS AND MIXED LINKED β-GLUCANS WHICH ARE LINEAR CELLULOSIC POLYMERS WITH 1,4- AND 1,3 LINKAGES.

HEMICELLULOSES HAVE CONSIDERABLY LOWER MOLECULAR WEIGHTS WITH DEGREES OF POLYMERIZATION BELOW 1.000. ONLY XYLOGLUCANS AND MIXED-LINKAGE β-GLUCANS REACH HIGHER DEGREES OF POLYMERIZATION COMPARABLE WITH THE ONES OF CELLULOSE. TWOFOLD HELICAL CONFORMATIONS (RIGHT-HANDED AND LEFT-HANDED) AS OBSERVED IN CELLULOSE ARE ALSO POSSIBLE FOR HEMICELLULOSES DUE TO THEIR STRUCTURAL SIMILARITY [JARVIS 2009]. DIFFERENCES BETWEEN CELLULOSE AND HEMICELLULOSES ARISE, BESIDE CONSTITUTIONAL DISTINCTION, ALSO FROM THE ABILITY TO FORM HYDROGEN BONDS. XYLANS ARE OFTEN SUBSTITUTED AT POSITIONS 2 AND 3 AND IN MANNANS, MOST OF THE HYDROXYL GROUPS IN POSITION 6 ARE BLOCKED WITH A GALACTOSE RESIDUE. MOREOVER FREE HYDROXYL GROUPS AT POSITION 2 OF MANNANS ARE NOT SUITABLE ORIENTATED TO GET IN CLOSE PROXIMITY WITH RESIDUES OF THE NEXT CHAIN.

THIS STRUCTURAL PECULIARITY TYPICALLY LEADS TO ONLY ONE HYDROGEN BOND NEXT TO THE GLYCOSIDIC LINKAGE, MAKING THEM MORE FLEXIBLE AND LESS LIKELY TO OCCUR IN SIMILAR CONFORMATION AS CELLULOSE. ONE REASON FOR THIS IS PROBABLY TO AVOID THE FORMATION OF MICROFIBRILS AMONG HEMICELLULOSE CHAINS WHICH IS NOT DESIRABLE FOR THEIR PHYSIOLOGICAL FUNCTION. NEVERTHELESS, THEIR STRUCTURAL CONFORMATION ALLOWS THE FORMATION OF HYDROGEN BONDS WITH CELLULOSE MICROFIBRILS ENHANCING THEIR MECHANICAL AND CHEMICAL STABILITY. DUE TO A REDUCED AMOUNT OF INTRA- AND INTERMOLECULAR HYDROGEN BONDS, HYDROXYL GROUPS WITHIN THE MOLECULE ARE BETTER ACCESSIBLE. THEREFORE, AND BECAUSE OF THROUGHOUT ACETYLATION OF THE POLYMER WITH AN AVERAGE DS OF 0.4-0.8 [JACOBS ET AL. 2002], THE ABILITY TO TAKE UP WATER IS SIGNIFICANTLY INCREASED, ENABLING WOOD SWELLING AND RESPONSIBLE FOR THE TYPICAL VISCOELASTICITY OF WOODEN MATERIALS [FAIX 2007].HEMICELLULOSES ARE LOCATED AROUND THE MICROFIBRILS OF CELLULOSE WHICH SERVE AS A SORT OF TEMPLATE FOR THEIR FORMATION. DUE TO THEIR ALIGNMENT ACCORDING TO THE CELLULOSE TEMPLATE, THEY SUBSEQUENTLY FORM THE TEMPLATE FOR LIGNIFICATION. THEIR GLUING CHARACTER AND THEIR CLOSE PROXIMITY TO CELLULOSE AND LIGNIN ARE THE REASON FOR THEIR CONSIDERATION AS THE GLUE WITHIN THIS NATURAL COMPOSITE MATERIAL [SALMEN AND OLSSON 1998].

LIGNIN

THE NAME LIGNIN CAN BE TRACED BACK AGAIN TO FRENCH CHEMIST ANSELM PAYEN, WHO ALSO INTRODUCED THE NAME CELLULOSE BY THE MIDDLE OF THE 19TH CENTURY. INITIALLY NAMED AS "THE TRUE WOODY MATERIAL" AND LATER ON "THE INCRUSTING MATERIAL", IT WAS FINALLY REFERRED AS LIGNUM OR LIGNIN [SCHUBERT 1965]. LIGNIN IS THE SECOND MOST ABUNDANT ORGANIC POLYMER ON EARTH ONLY SURPASSED BY CELLULOSE [FENGEL AND WEGENER 1989]. LIGNIN MAINLY CONSISTS OF THREE MONOMER SUBSTANCES WITH A PHENYLPROPANE CORE. THESE THREE BUILDING BLOCKS ARE *p*-COUMARYL (4-HYDROXY-CINNAMYL) ALCOHOL, CONIFERYL (3-METHOXY-4-HYDROXY-CINNAMYL), AND SINAPYL (3,5-DIMETHOXY-4-HYDROXY-CINNAMYL) ALCOHOL, TYPICALLY REFERRED AS H-, G- AND S-UNITS. THEIR COMMON STRUCTURE CAN BE TRACED BACK TO α-D-GLUCOSE AS PRECURSOR, TRANSFORMED IN THE SHIKIMIC ACID PATHWAY, SKETCHED IN **FIGURE 4**.
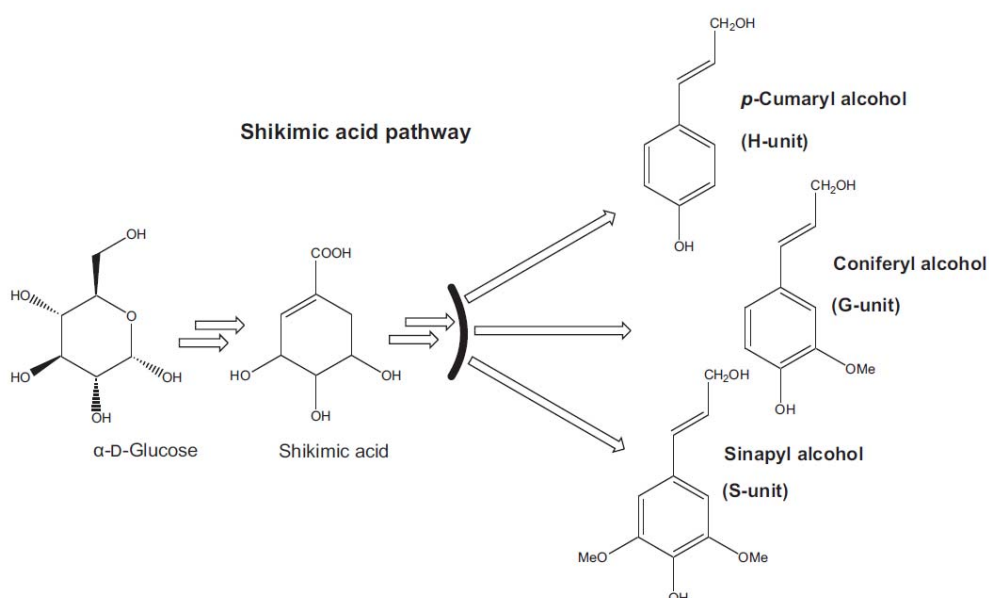

FIGURE 4. MOLECULAR STRUCTURE OF LIGNIN PRECURSORS

THEIR OCCURRENCE IN THE PLANT CELL WALL IS NOT BY RANDOM DISTRIBUTION BUT RATHER TYPICAL FOR SUPERIOR PLANT CATEGORIES. AS INDICATED IN **TABLE 2**, GRASSES SHOW HIGH AMOUNTS OF H-UNITS WHEREAS SOFTWOOD AND HARDWOOD HAVE ONLY SMALL SHARES. G-UNITS REPRESENT A CONSIDERABLE SHARE IN ALL CATEGORIES WITH MORE THAN 90 PERCENT IN SOFTWOOD. IN CONTRAST TO THIS, S-UNITS ARE ALMOST NON-EXISTENT IN SOFTWOOD LIGNIN BUT EQUALLY ABUNDANT TO G-UNITS IN GRASSES AND CAN REACH UP TO 75 PERCENT IN HARDWOOD BIOMASS.

TABLE 2. LIGNIN BUILDING BLOCK FREQUENCY IN TYPICAL LIGNOCELLULOSIC BIOMASS

LIGNIN SOURCE	GRASS [%]	SOFTWOOD [%]	HARDWOOD [%]
p-COUMARYL ALCOHOL	10-25	0.5-3.5	< 0.1
CONIFERYL ALCOHOL	25-50	90-95	25-50
SINAPYL ALCOHOL	25-50	0-1	50-75

Lignins are considered as polyphenols owing to their high amount of phenolic units. Compared with cellulose, lignins are inhomogeneous and irregular polymers with numerous possible linkages between its building blocks. **Figure 5** states some of the most common types of linkages among lignins but is not intended to be exhaustive.
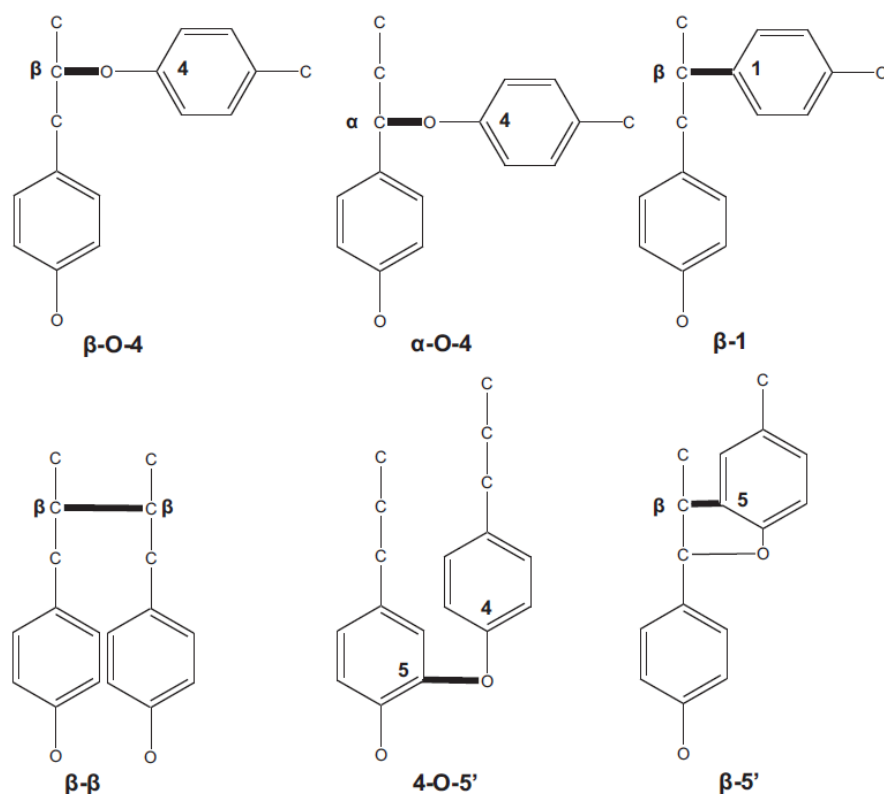
Figure 5. Common lignin linkages

These linkages are formed during the polymerization process which is an enzymatically induced radical reaction. Peroxidases and Laccases transform the lignin precursors into highly reactive phenoxyl radicals by utilizing strong oxidants as hydrogen peroxide or oxygen. These phenoxyl radicals subsequently react with each other and form the polymer called lignin. The lignification takes place around the hemicellulose template completing the composite material.

Lignins are in particular responsible for the mechanical strength and robustness of plants, especially in trees. External forces like gravity or pressure require a rigid material to allow growth and persistence under all environmental conditions. Especially horizontal growth like the formation of branches wouldn't be possible without the stabilizing properties of lignins. Their structure can also be drawn responsible for the viscoelastic properties of wooden material, which is another factor contributing to its high robustness [Faix 2007].

1.1.2 CONCEPTS

BIOREFINERY IS BASICALLY EVERYTHING THAT UTILIZES BIOMASS OR INTEGRATES BIOMASS CONVERSION PROCESSES AND LEADS TO THE PRODUCTION OF POWER AND VALUE-ADDED PRODUCTS. THE MOST EXHAUSTIVE DEFINITION HAS BEEN FORMULATED PREVIOUSLY BY THE INTERNATIONAL ENERGY AGENCY (IEA) BIOENERGY TASK 42 WITH: *"BIOREFINERY IS THE SUSTAINABLE PROCESSING OF BIOMASS INTO A SPECTRUM OF MARKETABLE PRODUCTS (FOOD, FEED, MATERIALS, CHEMICALS) AND ENERGY (FUELS, POWER, HEAT)"* [IEA 2008]. THE GENERAL INTENTION OF BIOREFINERY IS A STEPWISE REPLACEMENT OF THE PETROLEUM-BASED INDUSTRY PROVIDING A SIMILAR BUT SIGNIFICANTLY EXTENDED RANGE OF PRODUCTS.

ACCORDING TO THE IEA BIOENERGY TASK 42, BIOREFINERY CONCEPTS CAN BE CLASSIFIED BY FOUR MAIN FEATURES: PLATFORMS, PRODUCTS, FEEDSTOCK'S AND CONVERSION PROCESSES. PLATFORMS ARE REFERRED AS INTERMEDIATES (E.G. GAS, SUGARS) THAT CONNECT DIFFERENT SYSTEMS AND PROCESSES AND ARE AN INDICATOR FOR THE OVERALL SYSTEM COMPLEXITY. PRODUCTS ARE DISTINGUISHED INTO ENERGY PRODUCTS (E.G. BIOETHANOL, BIODIESEL, AND SYNTHETIC FUELS) AND MATERIAL PRODUCTS (E.G. CHEMICALS, MATERIALS, FOOD AND FEED). THE SUSTAINABLE RAW MATERIAL, ALSO REFERRED AS FEEDSTOCK, IS DIVIDED INTO ENERGY CROPS FROM AGRICULTURE (E.G. CROPS, SHORT ROTATION FORESTRY) AND BIOMASS RESIDUES FROM AGRICULTURE, FORESTRY, TRADE AND INDUSTRY (E.G. STRAW, BARK, USED COOKING OILS, WASTE STREAMS FROM BIOMASS PROCESSING). CONVERSION PROCESSES ARE THE FOURTH FEATURE WHEREBY BIOREFINERY CONCEPTS ARE CLASSIFIED. DEPOLYMERIZATION AND FRACTIONATION ARE THE MAIN TASKS AMONG OTHERS AND APPROACHED BY EITHER THERMO-CHEMICAL, BIOCHEMICAL, CHEMICAL AND MECHANICAL PROCESSES OR COMBINATIONS THEREOF.

THERMO-CHEMICAL PROCESSES AIM TO CONVERT BIOMASS INTO ENERGY AND CHEMICALS AT ELEVATED TEMPERATURES. DISTINCTIONS CAN BE MADE ACCORDING TO OXYGEN PRESENCE AND TEMPERATURE. GASIFICATION PROCESSES PROCEED AT LOW OXYGEN LEVELS AND TEMPERATURES ABOVE 700°C TO PRODUCE SYNGAS, A MIXTURE OF GASES, AS BIOFUEL OR PLATFORM FOR OTHER FUELS OR CHEMICALS [CHERUBINI 2010]. PYROLYSIS OCCURS UNDER COMPLETE EXCLUSION OF OXYGEN AT TEMPERATURES BETWEEN 300-600°C LEADING TO BIO-OIL, BIOCHAR AND SYNGAS. APPLICATIONS REACH FROM ELECTRIC POWER PRODUCTION OVER THERMAL ENERGY PLANTS TO BIOFUELS FOR MACHINES AND TRANSPORTATION.

BIOCHEMICAL PROCESSES UTILIZE MICROORGANISM AND/OR ENZYMES TO CONVERT FERMENTABLE SUBSTRATES IN LOW-MOLECULAR PRODUCTS THROUGH FERMENTATION OR AEROBIC DIGESTION. THESE PROCESSES PROCEED TYPICALLY AT LOWER TEMPERATURES

AT OR AROUND THE IDEAL CONDITIONS OF THE BIOACTIVE CATALYSTS CURRENTLY ALMOST EXCLUSIVELY AIMING FOR BIOETHANOL (AEROBIC) OR BIOGAS (ANAEROBIC) PRODUCTION.

CHEMICAL PROCESSES ARE ALL PROCESSES THAT TRANSFORM SUBSTRATES OR INTERMEDIATES BY REACTION WITH ONE OR MORE REACTANTS. MOST COMMON REACTIONS ARE ACID OR ALKALINE CATALYZED HYDROLYSIS OF POLYSACCHARIDES OR TRANSESTERIFICATION OF OILS FOR BIOFUEL PRODUCTION BUT CAN ALSO INCLUDE ALL OTHER REACTIONS KNOWN TO THE CHEMIST.

MECHANICAL PROCESSES ARE THE MOST ELEMENTARY PROCESSES OF EVERY BIOREFINERY CONCEPT TYPICALLY AT THE BEGINNING OF THE OPERATION CHAIN. SIZE REDUCTION AND SEPARATION STEPS CAN BE FOUND IN ALMOST EVERY WOOD-BASED BIOREFINERY CONCEPT TO PROVIDE THE RAW MATERIAL IN SUITABLE SHAPE AND CONSTITUTION. BUT ALSO PHYSICAL PROCESSES LIKE EXTRACTION OR VARIOUS PRE-TREATMENT METHODS TO ACHIEVE LIGNOCELLULOSE SEPARATION INTO ITS MAIN COMPONENTS, CELLULOSE, HEMICELLULOSES AND LIGNIN, FALL WITHIN THIS CATEGORY [CHERUBINI 2010].

CLASSIFICATION OF BIOREFINERY SYSTEMS TYPICALLY PROCEEDS BY SPECIFYING THE SYSTEM ACCORDING TO THE FIRST THREE FEATURES. INFORMATION ABOUT INVOLVED PROCESSES CAN BE ADDED IF REQUIRED FOR CLARITY BUT IS USUALLY OMITTED.

EXAMPLES GIVEN BY THE IEA TASK 42 ARE AS FOLLOWS [IEA 2008]:

♦ LIGNIN BIOREFINERY FOR BIOMATERIALS, ELECTRICITY AND HEAT FROM LIGNOCELLULOSIC CROPS OR RESIDUES (ZELLSTOFF STENDAL GMBH, GERMANY)

♦ C6/C5 SUGARS AND LIGNIN BIOREFINERY FOR BIOETHANOL, CHEMICALS AND BIOMATERIALS FROM LIGNOCELLULOSIC CROPS OR RESIDUES (LIGNOL INNOVATIONS LTD., CANADA)

♦ OIL AND ORGANIC SOLUTION BIOREFINERY FOR BASE-CHEMICALS, BIODIESEL, POWER AND/OR HEAT FROM MICRO-ALGAE (WUR MICRO-ALGAE BIOREFINERY, NETHERLANDS)

♦ PYROLYTIC LIQUID BIOREFINERY FOR FOOD FLAVOURINGS, POLYMERS, FUELS AND HEAT FROM LIGNOCELLULOSIC RESIDUE (ENSYN, CANADA)

THESE EXAMPLES SHOW THAT THERE ARE ALREADY VARIOUS BIOREFINERY CONCEPTS AVAILABLE ALTHOUGH MOST ARE STILL FAR FROM COMMERCIALIZATION BUT SEVERAL ARE EXPECTED TO BE ESTABLISHED IN THE FUTURE. **FIGURE 6** GIVES A COMPREHENSIVE OVERVIEW OF CURRENTLY EXISTING CONCEPTS AND THEIR CONNECTION POINTS TO OTHERS WITH THE FOUR MAIN GROUPS OF PROCESSES HIGHLIGHTED IN COLOR.
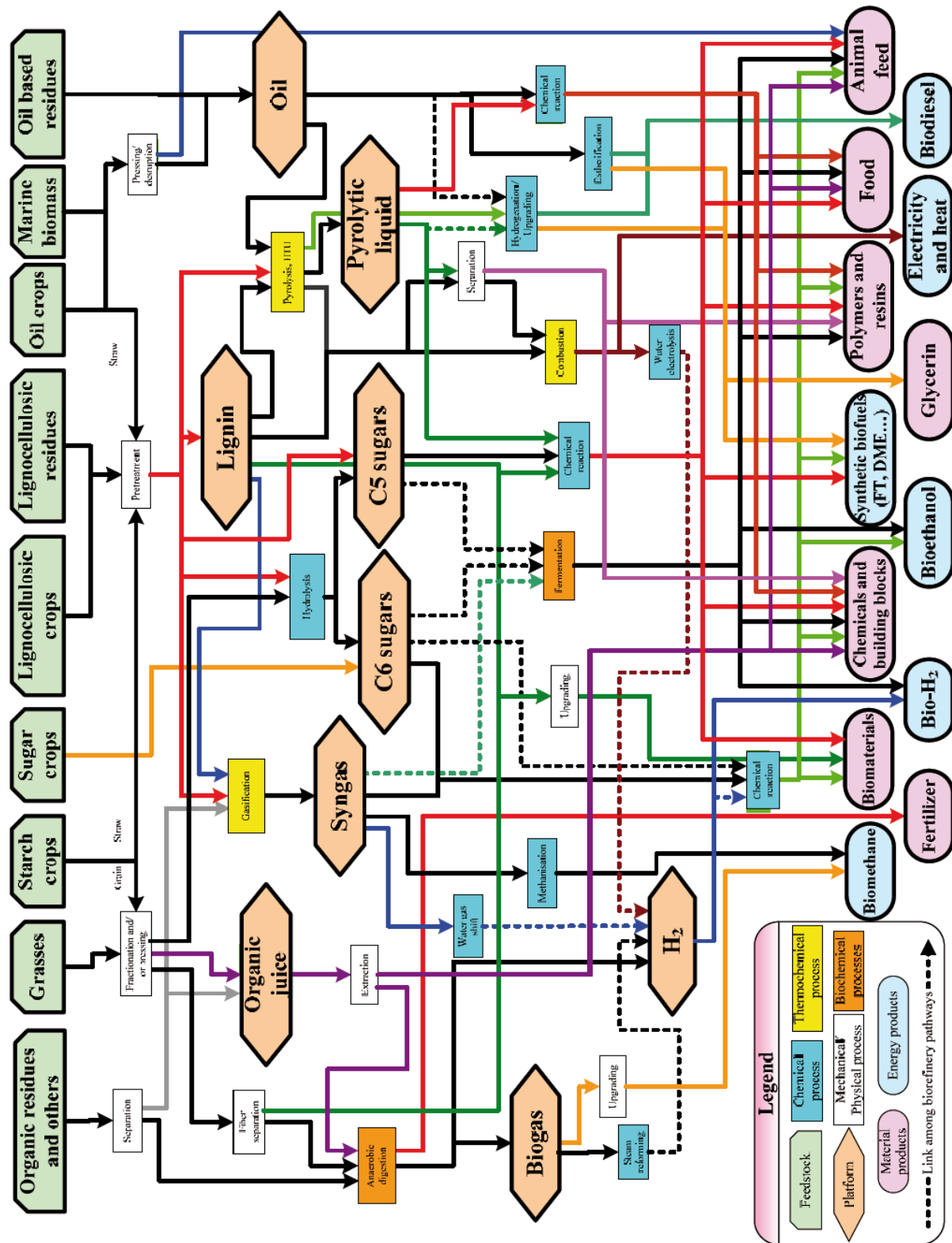
FIGURE 6. OVERVIEW OF CURRENT PLATFORMS, PRODUCTS, FEEDSTOCK'S AND PROCESSES ACCORDING TO THE IEA TASK 42 BIOREFINERY CLASSIFICATION SYSTEM. DIFFERENT PROCESSES ARE HIGHLIGHTED IN COLOR: THERMO-CHEMICAL (YELLOW), BIOCHEMICAL (RED), CHEMICAL (BLUE) AND MECHANICAL (WHITE) [IEA 2008].

IN THE NEAR FUTURE, IMPLEMENTATION OF NEW BIOREFINERY CONCEPTS CAN BE EXPECTED TO A CONSIDERABLE DEGREE. BOTH, UPGRADING OF EXISTING INDUSTRIAL INFRA-STRUCTURES OR CONSTRUCTION OF NEW LARGE SCALE PRODUCTION SITES WILL TAKE PLACE WITHIN THE NEXT DECADE. OBSTACLES ON THE WAY TO A BROAD GLOBAL CHANGE IN TECHNOLOGY ARE STILL TOO LOW OIL PRICES AND THE GLOBAL FINANCIAL INSTABILITY MAKING BIG INVESTMENTS CHALLENGING AND PRICE COMPETIVENESS A DISTANT GOAL.

BIOREFINERY PLATFORM PRODUCTS WILL BE DIFFERENT TO THOSE AVAILABLE FROM PETROCHEMICAL INDUSTRY TODAY DUE TO A DIFFERENT STRUCTURE OF THE RAW MATERIAL AND A CONSIDERABLY HIGHER OXYGEN CONTENT. BASICALLY ALL OIL REFINERY PLATFORM CHEMICALS CAN BE OBTAINED FROM BIOMASS PROCESSING BUT LOWER YIELDS ASSOCIATED WITH HIGHER COSTS MAKE ONLY A LIMITED NUMBER PROFITABLE. OTHER OTHERWISE TOO EXPENSIVE PLATFORM CHEMICALS CAN BE DERIVED FROM THESE PRODUCTS BY SUBSEQUENT TRANSFORMATION. SO FAR, CELLULOSE AND HEMICELLULOSES FROM LIGNOCELLULOSIC FEEDSTOCK'S ARE EXPECTED TO PLAY THE MAJOR ROLE IN THE BIOREFINERIES ON A SHORT AND MIDDLE TERM PERSPECTIVE. THEY ARE EASILY ACCESSIBLE AND CONVERTIBLE TO NUMEROUS PLATFORM CHEMICALS AS MONOSUGARS, ITS DERIVATIVES AND OTHER VALUE-ADDED PRODUCTS.

THE MOST PROMISING FUTURE CANDIDATES FOR BIOMASS DERIVED PLATFORM CHEMICALS HAVE BEEN COMPILED BY THE U.S. DEPARTMENT OF ENERGY IN 2004 (**TABLE 3**) NOT TAKING ETHANOL INTO ACCOUNT, AS IT IS ALREADY TARGET OF EXTENSIVE INVESTIGATION MAINLY FOCUSING ON THE BIOFUEL SECTOR [CHERUBINI 2010].

TABLE 3. TOP 30 BIOMASS PLATFORM MOLECULES [WERPY AND PEDERSEN 2005].

CARBON NUMBER	POTENTIAL TOP 30 CANDIDATES
1	CARBON MONOXIDE & HYDROGEN (SYNGAS)
2	NONE
3	GLYCEROL, 3-HYDROXYPROPIONIC ACID, LACTIC ACID, MALONIC ACID, PROPIONIC ACID, SERINE
4	ACETOIN, ASPARTIC ACID, FUMARIC ACID, 3-HYDROXYBUTYROLACTONE, MALIC ACID, SUCCINIC ACID, THREONINE
5	ARABINITOL, FURFURAL, GLUTAMIC ACID, ITACONIC ACID, LEVULINIC ACID, PROLINE, XYLITOL, XYLONIC ACID
6	ACONITIC ACID, CITRIC ACID, 2,5-FURAN DICARBOXYLIC ACID, GLUCARIC ACID, LYSINE, LEVOGLUCOSAN, SORBITOL

1.2 IONIC LIQUIDS

"IONIC LIQUIDS MAY BE VIEWED AS A NEW AND REMARKABLE CLASS OF SOLVENTS, OR AS A TYPE OF MATERIALS THAT HAVE A LONG AND USEFUL HISTORY. IN FACT, IONIC LIQUIDS ARE BOTH, DEPENDING ON YOUR POINT OF VIEW" [WILKES 2003].

ALTHOUGH IONIC LIQUIDS APPEAR NEW TO SOME, THEY ARE IN FACT SUBJECT OF STUDY FOR QUITE A WHILE. WHAT HAS CHANGED WITHIN THE LAST ONE OR TWO DECADES IS THE EXTEND OF INTEREST IN THIS RESEARCH TOPIC. UNTIL 1995, THE ANNUAL OUTPUT OF SCIENTIFIC PUBLICATIONS CONCERNING OR INCLUDING IONIC LIQUIDS REMAINED CONSTANT AT ABOUT TWENTY. IN THE NEXT YEARS, UNTIL THE START OF THE NEW MILLENNIUM IN 2001, A SIGNIFICANT INCREASE IN INTEREST CAN BE OBSERVED ALMOST REACHING THE TENFOLD OF 1997. WITHIN THE FOLLOWING DECADE THESE NUMBER EXPLODED TO ALMOST SIX THOUSAND ABSTRACTS BY 2010, INDICATED IN **FIGURE 7**.
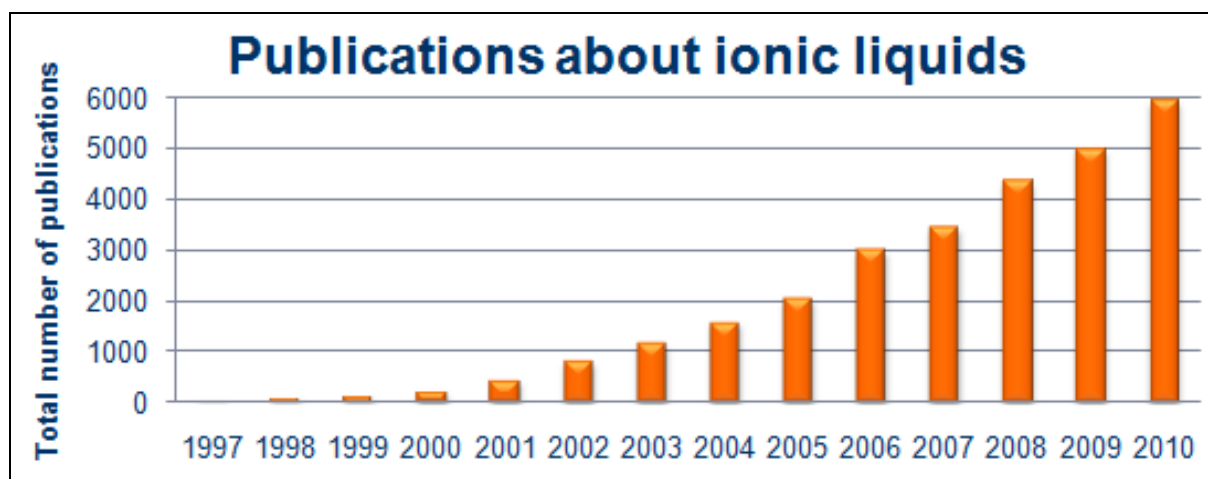

*FIGURE 7. ANNUALLY PUBLISHED ABSTRACTS ABOUT IONIC LIQUIDS IN THE RECENT PAST (**SCI**-FINDER).*

THE FAST PROGRESS IN THIS SCIENTIFIC AREA CAN BE EXPLAINED WITH THE REALIZATION, THAT IONIC LIQUIDS, ROOM-TEMPERATURE IONIC LIQUIDS (RTILS), NONAQUEOUS IONIC LIQUIDS, MOLTEN SALTS, LIQUID ORGANIC SALTS OR FUSED SALTS AS THEY ARE ALSO CALLED, CAN BE USED MEANINGFUL FOR ALL KIND OF APPLICATIONS BESIDE THEIR INITIAL APPLICATION FOR ELECTROCHEMICAL PURPOSES. THEIR PARTIALLY UNIQUE PROPERTIES AND THE ABILITY TO DESIGN CUSTOM MADE SOLVENTS AND REACTANTS THROUGH AN INFINITE NUMBER OF POSSIBLE ION-PAIR COMBINATIONS MADE THEM INCREASINGLY INTERESTING FOR MANY SCIENTIFIC AREAS. IONIC LIQUIDS CONTRIBUTED TO SOLVE LONGSTANDING PROBLEMS, OVERCOME OBSTACLES AND EVEN OPENED UP NEW SCIENTIFIC AREAS WHICH COULDN'T BE ACCESSED BEFORE. IF THE CURRENT PROGRESSIVITY IN IONIC LIQUIDS CONTINUES OR INCREASES EVEN FURTHER, MANY NEW AND EXCITING FACTS WILL BE UNVEILED AND MEANINGFUL APPLICATIONS FOUND.

1.2.1 HISTORY

THE FIRST APPEARANCE OF AN IONIC LIQUID WAS AS EARLY AS IN THE MIDDLE OF THE 19TH CENTURY IN FORM OF AN "RED OIL" OCCURRING AS SIDE PRODUCT OF FRIEDL-CRAFTS REACTIONS BETWEEN BENZENE AND CHLOROMETHANE [WILKES 2002]. MORE THAN ONE HUNDRED YEARS LATER AND WITH THE INVENTION OF NMR-SPECTROSCOPY, THIS OIL COULD BE IDENTIFIED AS THE SIGMA-COMPLEX, A LONG-PRESUMED STABLE REACTION INTERMEDIATE CONSISTING OF A BENZENE-CATION AND AN HEPTACHLORODIALUMINATE-ANION RENDERING THIS CATION-ANION COMBINATIONS AS THE FIRST IONIC LIQUID IN HISTORY (SEE **FIGURE 8**).
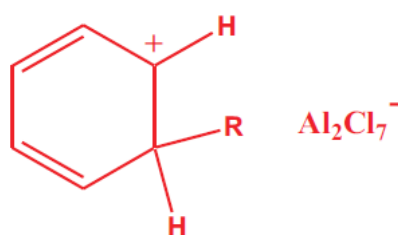
FIGURE 8. THE "RED OIL" IL [WILKES 2002]

THE NEXT REPORT ABOUT EARLY IONIC LIQUIDS WAS IN 1914 BY WALDEN WITH THE SYNTHESIS OF ALKYL AMMONIUM NITRATES CALLED FUSED SALTS AT THIS TIME [WALDEN 1914]. THE FIRST REPORT ABOUT AN IONIC LIQUID AS WE USE TODAY IS FROM A PATENT IN 1948 [HURLEY 1948]. THE DESCRIBED IONICALLY CONDUCTING MIXTURES OF AlCl$_3$ AND 1-ETHYLPYRIDINIUM HALIDES ARE ALREADY A CONVERSANT CATION-ANION COMBINATION CONSISTING OF AN ORGANIC CATION COMBINED WITH AN INORGANIC COUNTERION ONLY DIFFERING BY THEIR BINARY CHARACTER THROUGH THE ALUMINUM SALT ADDITIVE TO IONIC LIQUIDS OF TODAY. IN THE 1960S, FURTHER SALTS WITH A MELTING POINT AT OR NEAR ROOM TEMPERATURE HAVE BEEN DETECTED BY YOKE ET AL. CONSISTING OF A COPPER(I) CHLORIDE AND ALKYL AMMONIUM CHLORIDE MIXTURE. ALTHOUGH BOTH EDUCTS ARE SOLIDS AT ROOM TEMPERATURE, THEY FORM A LIQUID WITH THE MOLECULAR FORMULA Et$_3$NHCuCl$_2$ WHEN MIXED [YOKE ET AL. 1963]. REMARKABLE IN THIS CONTEXT IS THE REPEATING OCCURRENCE OF ALKYL AMMONIUM CATIONS WHICH ARE NOWADAYS IN A SLIGHTLY DIFFERENT CONSTITUTION THE MOST PROMINENT CATIONS AMONG MODERN, SECOND GENERATION ROOM TEMPERATURE IONIC LIQUIDS. ALTHOUGH E.G. ETHYL AMMONIUM NITRATE HAS A MELTING POINT AT 12°C WHEREFORE THE TERM ROOM TEMPERATURE IONIC LIQUID WOULD APPLY, THESE MOLTEN SALTS HAVE NOT MUCH IN COMMON WITH THE IONIC LIQUIDS AVAILABLE TODAY. IN THE 1970S, ATWOOD AND ATWOOD [1976] PRESENTED A STUDY ABOUT LIQUID CLATHRATES; INCLUSION COMPOUNDS CONSISTING OF A MOLECULAR LATTICE AND AN INCLUDED TRAPPED MOLECULE. THESE ALUMINUM CLATHRATES HAVE THE MOLECULAR FORMULA M[Al$_2$(CH$_3$)$_6$X], WHERE M STANDS FOR INORGANIC OR ORGANIC CATION AND X FOR HALIDES IN GENERAL. EVEN THOUGH

RAPPROCHEMENT TOWARDS MODERN IONIC LIQUID THROUGH THE INCREASING WEIGHT OF AN ORGANIC CATION CAN BE OBSERVED, NONE OF THESE MOLTEN SALTS ARE CLOSE TO WHAT WE REFER AS SUCH TODAY.

THE BIRTH OF MODERN IONIC LIQUIDS, OFTEN REFERRED AS SECOND GENERATION IONIC LIQUIDS, WAS IN THE LATE 1980S AT THE U.S. AIR FORCE ACADEMY IN SEARCH OF NEW ELECTROLYTES FOR THERMAL BATTERIES. THIS PROJECT, INITIATED IN THE 1960S UNDER MAJOR (DR.) LOWELL A. KING, WAS INITIALLY FOCUSED ON THE UTILIZATION OF BINARY MIXTURES OF MAINLY INORGANIC SALTS SIMILAR THAN ALL OF THEIR PREDECESSORS DID. AFTER INTENSIVE INVESTIGATION OF CURRENT LITERATURE ABOUT ALUMINUM ELECTROPLATING, THE PUBLICATION FROM HUSSEY OUT OF 1948 CAUGHT THEIR ATTENTION. THIS WAS THE TIME WHEN PEOPLE AROUND CAPTAIN (DR.) JOHN S. WILKES AND PROF. CHARLES HUSSEY STARTED TO INVESTIGATE ORGANIC CATIONS, PARTICULARLY ALKYLPYRIDINIUM CATIONS, INTO MORE DETAIL [WILKES ET AL. 1982]. LATER ON THEY FOUND 1-ETHYL-3-METHYL-IMIDAZOLIUM CATIONS APPLICABLE AS SOLVENTS AND CATALYSTS [BOON ET AL. 1986] BUT IT WAS NOT UNTIL THE 1990S, WHEN THE FIRST WATER-STABLE IONIC LIQUIDS, THE ONE WE USE TODAY, HAVE BEEN INTRODUCED BY WILKES AND ZAWOROTKO [1992].

ALL PREVIOUS MOLTEN SALTS HAD TO BE HANDLED WITH UTMOST CARE IN AN INERT GAS ATMOSPHERE, TYPICALLY PROVIDED IN A GLOVE BOX, AS THEY ALL WERE EXTREMELY SENSITIVE TO WATER. COUNTER-IONS AS TETRAFLUOROBORATE, HEXAFLUOROPHOSPHATE, NITRATE, SULFATE AND ACETATE OF DIALKYLIMIDAZOLIUM CATIONS TURNED OUT TO BE PREPARED READILY AND TO BE HANDLED OUTSIDE A GLOVE-BOX [WILKES 2003]. ESPECIALLY THE SIMPLIFIED HANDLING SIGNIFICANTLY INCREASING THEIR APPLICABILITY AND THUS CAN BE DRAWN RESPONSIBLE FOR THE SUBSEQUENT RISE OF INTEREST WHICH HAD ITS ORIGIN DEMONSTRABLY IN THE MIDDLE OF THE 1990S. NOTEWORTHY IN THIS REGARD IS ALSO THE WORK OF FISCHER ET AL. ON INORGANIC MOLTEN SALTS [1999; 2003]. PARTICULARLY LITHIUM BASED METAL SALT HYDRATES WITH A MELTING POINT BELOW 100°C AND THEIR ABILITY TO DISSOLVE CELLULOSE RENDER THEM AS COMPARABLE SOLVENT SYSTEMS ALSO FULFILLING THE BASIC REQUIREMENTS FOR IONIC LIQUIDS (E.G. mp < 100°C; NON-VOLATILE, ETC.).

ALTHOUGH IONIC LIQUIDS HAVE BEEN AROUND SINCE 150 YEARS OR MORE, THEIR STORY WE TELL TODAY STARTED WITH THEIR REBIRTH LESS THAN TWO DECADES AGO STILL RENDERING THEM AS A NEW AND UPCOMING RESEARCH AREA WITH MANY SECRETS TO BE UNCOVERED.

1.2.2 STRUCTURE

IONIC LIQUIDS ARE BASICALLY NOTHING MORE THAN ORGANIC SALTS THAT, IN CASE OF ROOM TEMPERATURE IONIC LIQUIDS USED TODAY, HAVE A LOW MELTING NEAR OR AT ROOM TEMPERATURE BUT PER DEFINITION DEFINITELY BELOW 100°C. THE MAIN DIFFERENCE TO INORGANIC SALTS E.G. SODIUM CHLORIDE, IS THEIR ORGANIC CATION WHICH CAN BE DRAWN RESPONSIBLE FOR A SIGNIFICANTLY LOWERED MELTING POINT. IONIC LIQUIDS ARE FULLY IONIZED FLUIDS CONSISTING OF AN INFINITE NUMBER OF POSSIBLE CATION-ANION COMBINATIONS LIMITED ONLY BY OUR IMAGINATION; A PHRASE JOHN S. WILKES USED FOR THE DESCRIPTION OF THEIR APPLICATION POTENTIAL [WILKES 2003]. CATIONS ARE TYPICALLY LESS LIKELY TO BE VARIED WITH THE MOST IMPORTANT ONES BY TODAY PRESENTED IN **FIGURE 9**.
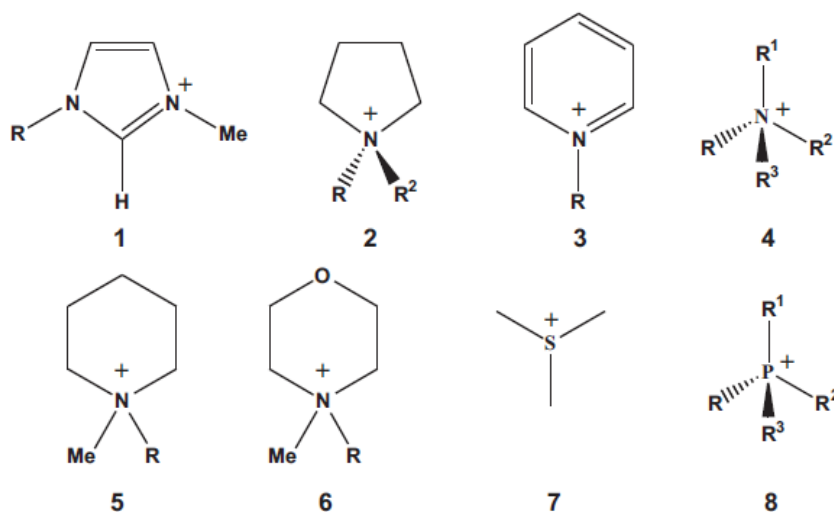

FIGURE 9. MOST IMPORTANT IONIC LIQUID CATIONS: 1: 1-ALKYL-3-METHYLIMIDAZOLIUM; 2: 1,1-DIALKYLPYRROLIDINIUM; 3: 1-ALKYLPYRIDINIUM; 4: TETRAALKYLAMMONIUM; 5: 1-ALKYL-1-METHYLPIPERIDINIUM; 6: 1-ALKYL-1-METHYMORPHOLINIUM; 7: TRIALKYLSULFONIUM; 8: TETRAALKYLPHOSPHONIUM

ALL OF THESE CATIONS EXCEPT THE SULFONIUM-BASED ONES ARE QUATERNARY COMPOUNDS WITH NITROGEN AS PREVAILING CORE ATOM. AMONG THESE IONIC LIQUID FAMILIES, THE FIRST MENTIONED 1-ALKYL-3-METHYLIMIDAZOLIUM IS BY FAR THE MOST COMMONLY USED WITH NUMEROUS VARIATIONS OF THE ALKYL CHAIN LENGTH. THE ELECTRONIC STRUCTURE CAN BE DESCRIBED BEST WITH A 3-CENTER-4-ELECTRON CONFIGURATION ACROSS THE N_1-C_2-N_3 MOIETY, A DOUBLE BOND BETWEEN C_4 AND C_5 VIS-À-VIS AND A WEAK DELOCALIZATION IN THE CENTER OF THE AROMATIC RING [WEINGÄRTNER 2008]. THE C_2-H BOND IS FREQUENTLY STATED TO BE MORE ACIDIC THAN $C^{4/5}$-H BUT OFTEN MISTAKENLY ARGUED WITH THE HIGHER ACIDITY OF THE RESPECTIVE HYDROGEN. HUNT ET AL. [2006] DEMONSTRATED WITH AB INITIO CALCULATIONS THAT THE ALSO EXPERIMENTALLY CONFIRMED GREATER ACIDITY OF THE C_2 HYDROGEN ARISES FROM THE CHARGE OF THE C-H MOIETY AND CANNOT BE REDUCED TO THE RING HYDROGEN'S ALONE. THIS FINDING IS CONSIDERED VERY IMPORTANT TO UNDERSTAND ITS NATURE.

IONIC LIQUID ANIONS ARE WAY MORE DIVERSE THAN THEIR CATIONIC COUNTERPARTS WITH A WIDE RANGE OF COMMERCIALLY AVAILABLE CATION-ANION COMBINATIONS AND EVEN MORE TO BE FOUND IN LITERATURE. LITERALLY EVERY MOLECULE WITH A NEGATIVE CHARGE, ORGANIC OR INORGANIC, CAN BECOME IN THE SIGHTS OF INVESTIGATION. HOWEVER, MOST STUDIES, ESPECIALLY THE ONE LOOKING FOR POTENTIAL APPLICATIONS, ARE FOCUSED ON A LIMITED NUMBER OF ANIONS WITH A SELECTION OF THE MOST COMMON ONES GIVEN IN **FIGURE 10**.
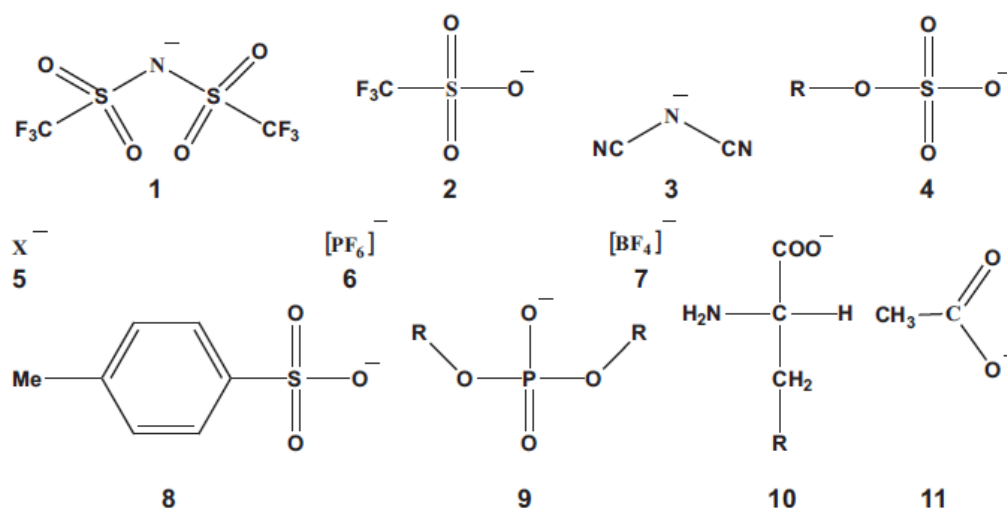
FIGURE 10. SELECTION OF MOST COMMON IONIC LIQUID ANIONS: 1: BIS(TRIFLUOROMETHANESULFONYL)IMIDE; 2: TRIFLUOROMETHANESULFONATE; 3: DICYANIMIDE; 4: ALKYLSULFATES; 5: HALIDES; 6: HEXAFLUOROPHOSPHATE; 7: TETRAFLUOROBORATE; 8: TOSYLATE; 9: DIALKYLPHOSPHATE; 10: AMINO ACIDS; 11: ACETATE

BIS(TRIFLUOROMETHANESULFONYL)IMIDE, OFTEN SIMPLY REFERRED AS BISIMIDE, IS ONE OF THE MOST COMMONLY USED ANIONS AS THEIR COMBINATIONS ARE READILY TO PREPARE AND LEAD TO DESIRABLE IONIC LIQUIDS FEATURES AS LOW VISCOSITY OR HIGH THERMAL AND ELECTROCHEMICAL STABILITY [BONHOTE ET AL. 1996]. PERFLUORINATION WAS FOUND TO BE RESPONSIBLE FOR THESE FEATURES RENDERING TRIFLUOROMETHANESULFONATE AS AN EQUALLY PERFORMING ANION [PRINGLE ET AL. 2003]. OTHER MORE COMPLEX ANIONS LIKE DICYANIMIDE, ALKYLSULFATES, DIALKYLPHOSPHATES OR TOSYLATES ARE GOING TO REPLACE THE INITIALLY PREFERRED HALIDES DUE TO LESS UNFAVORABLE PROPERTIES. HALIDES SHOW SEVERE DISADVANTAGES ARISING FROM THEIR STRONGLY HYDROSCOPIC AND OFTEN CORROSIVE CHARACTER. HEXAFLUOROPHOSPHATE AND TETRAFLUOROBORATE ARE WIDELY USED IONIC LIQUID ANIONS BUT LACKING IN HYDROLYTIC STABILITY MAKING THEM LESS APPLICABLE FOR A WIDE RANGE OF OTHERWISE POSSIBLE APPLICATIONS [FONSECA ET AL. 2003]. AMINO ACID IONIC LIQUIDS ARE LESS COMMON ONES BUT COME WITH INTERESTING FEATURES. THEIR MISCIBILITY WITH ORGANIC SOLVENTS AND ABILITY TO DISSOLVE UNMODIFIED AMINO ACIDS UNDER NON-AQUEOUS CONDITIONS MAKE THEM INTERESTING TARGETS FOR FUTURE STUDIES [FUKUMOTO ET AL. 2005]. THE ACETATE ANION IS ONE OF THE MOST OFTEN USED ANIONS IN IONIC LIQUID ENHANCED BIOREFINERY AS 1-ALKYL-3-METHYLIMIDAZOLIUM COUNTER-ION. IT'S ABILITY TO DISSOLVE BIOREFINERY PRODUCTS SUCH AS CELLULOSE, LIGNIN AND HEMICELLULOSES IN THEIR GENUINE FORM

WITHOUT ANY PRIOR DERIVATIZATION AND AT CONSIDERABLY HIGH CONCENTRATION AND EVEN NON-MODIFIED WOOD, RENDERS THEM AS A UNIQUE CLASS OF ION-PAIRS WITH NUMEROUS POTENTIAL APPLICATIONS [SWATLOSKI ET AL. 2002; KILPELAINEN ET AL. 2007].

THE MOLECULAR STRUCTURE OF IONIC LIQUIDS IS DOMINATED BY LONG-RANGE COULOMB FORCES EMERGING BETWEEN NET CHARGES OF THE IONS. THESE FORCES TEND TO DECREASE IN LARGER ION-PAIRS REPLACED BY HIGHLY DIRECTIONAL INTERACTIONS OF SHORTER RANGE, IN DEPENDENCE OF THE ION SPACING [WEINGÄRTNER 2008]. DIPOLE-DIPOLE FORCES ARE THE PREVAILING ELECTROSTATIC INTERACTIONS IN SUCH MOLECULAR LIQUIDS DETERMINING THE DIELECTRIC CONSTANT OF THE SOLVENT AND THE INTERACTION WITH POTENTIAL SOLUTES. X-RAY AND NEUTRON SCATTERING EXPERIMENTS UNVEILED LONG-RANGE, CHARGE-ORDERED STRUCTURES FOR IMIDAZOLIUM-TYPE IONIC LIQUID SYSTEMS WITH ALTERNATING LAYERS OF CATIONS AND ANIONS BUILDING THE MOLECULAR BACKBONE IN SOLID STATE [DEETLEFS ET AL. 2006]. THIS FINDING TENDS TO BECOME LESS APPLICABLE IN THE LIQUID STATE AS A CONSEQUENCE OF THE INHERENT FLEXIBILITY OF THE ANION. MOREOVER LARGE ANIONS E.G. BIS(TRIFLUOROMETHANESULFONYL)IMIDE WERE FOUND TO BE LESS LIKELY LEADING TO CHARGE ORDERED STATES THAN SMALLER ANIONS AS HALIDES OR HEXAFLUOROPHOSPHATE.

THE RELATIVE POSITION OF THE IONS TO EACH OTHER IS STRONGLY DEPENDENT ON THE STEREOCHEMISTRY. IN CASE OF IMIDAZOLIUM-TYPE CATIONS, SMALL ANIONS LIKE CHLORIDE WERE FOUND TO ALLOW SEVEN STABLE STRUCTURES WITH THE POSSIBLE ANION POSITIONS CALLED: FRONT-METH, FRONT-BUT, TOP (AND THUS BOTTOM), BUT-SIDE, METH-SIDE AND BACK, PICTURED IN **FIGURE 11**.
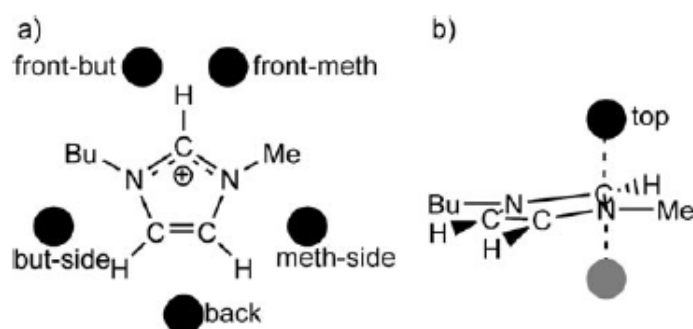

FIGURE 11. LOCATION OF PRIMARY CATION-ANION INTERACTION SITES FOR [C_4C_1im]Cl: A) Cl ANION IN-PLANE; B) Cl ANION OUT-OF-PLANE [HUNT ET AL. 2006].

TOP AND FRONT CONFORMERS HAVE BEEN IDENTIFIED AS THE LOWEST IN ENERGY AND ARE THEREFORE THE MOST PROBABLE LOCATIONS FOR THE NEGATIVELY CHARGED ANION [HUNT ET AL. 2006]. BULKY ANIONS LIKE THE BIS(TRIFLUOROMETHANESULFONYL)IMIDE WERE FOUND TO HAVE HIGHEST PROBABILITIES AT POSITIONS ASSOCIATED WITH THE FACE OF THE RING SYSTEM WITH OUT-OF-PLANE LOCATIONS VERY UNLIKELY [DEETLEFS ET AL. 2006].

RATHER UNCLEAR REMAINS THE ACTUAL RELATIONSHIP OF THE IONS IN THE LIQUIDS STATE AND THEIR COORDINATION ON A MESOSCOPIC LEVEL. UNTIL TODAY, IT COULD NOT BE SHOWN DOUBTLESS IF SUCH CATION-ANION COMBINATIONS GENERATE A FULLY DISSOCIATED SYSTEM OR ARE MORE LIKELY TO FORM ION-PAIRS. ANOTHER TOPIC OF SCIENTIFIC DISCOURSE IS THE EXISTENCE OF MESOSCOPIC STRUCTURES AS STRUCTURAL DOMAINS OR OTHER SUPRAMOLECULAR COORDINATION STRUCTURES EXCEEDING THE SINGLE ATOM SCALE [WEINGÄRTNER 2008].

THESE UNCERTAINTIES ABOUT FUNDAMENTAL ASSEMBLY OF THE OBJECT OF STUDY ARISE FROM THE RATHER SHORT HISTORY OF INTENSIVE INVESTIGATION AND GIVE RISE TO CONTINUE ON THE WAY TO ENTIRE UNDERSTANDING AND FULL CONTROLLABILITY OF IONIC LIQUIDS PROPERTIES, WHICH WILL BE DISCUSSED IN THE NEXT CHAPTER.

1.2.3 PHYSICOCHEMICAL PROPERTIES

THERMAL BEHAVIOR

IONIC LIQUIDS HAVE A QUITE INTERESTING THERMAL BEHAVIOR ON BOTH ENDS OF THE LIQUID STATE. TO DIFFERENTIATE IONIC LIQUIDS FROM MOLTEN SALTS, THEY HAVE TO HAVE A MELTING POINT BELOW 100°C AND AROUND 25°C TO BE CONSIDERED AS ROOM TEMPERATURE IONIC LIQUIDS. A SIGNIFICANT DIFFERENCE OF IONIC LIQUIDS TO COMMON MOLECULAR SOLVENTS IS THEIR TYPICALLY LARGE LIQUIDUS RANGE STRETCHING OVER SEVERAL HUNDRED DEGREES. LIMITATION ARISES THROUGH GLASS FORMATION AT LOW TEMPERATURES WHICH CAN BE AS LOW AS -100°C BUT TYPICALLY FURTHER UP THE TEMPERATURE SCALE. CRYSTALLIZATION WAS FOUND ENERGETICALLY NOT OVERLY FAVORED BUT CAN OCCUR AS A CONSEQUENCE OF SOLID STATE POLYMORPHISM [HOLBREY AND ROGERS 2003]. THE MELTING POINT IS DESCRIBED BEING DEPENDENT ON THREE MAJOR CHARACTERISTICS: CHARGE, SIZE AND CHARGE DISTRIBUTION, WHICH CAN BE STEERED BY VARIATION OF CATIONS AND ANIONS. THIS ADJUSTABILITY OF IONIC LIQUID PROPERTIES WITHIN LIMITS APPLIES TO ALL PHYSICOCHEMICAL PROPERTIES AND IS ONE OF THEIR UNIQUE FEATURES RESPONSIBLE FOR THE RAPIDLY INCREASING INTEREST IN THIS TOPIC. THE OVERALL LATTICE ENERGY OF IONIC SOLIDS WAS FOUND TO BE DEPENDENT ON A PRODUCT OF THREE ION TRAITS BEING THE NET ION CHARGES, THEIR SEPARATION AND THEIR PACKING EFFICIENCY. AS A CONSEQUENCE, LOW MELTING POINTS SHOULD OCCUR WHEN ION CHARGES ARE ±1 AND THE IONS ARE LARGE AND THUS ENABLE FAR INTER-ION SEPARATION AND CHARGE DELOCALIZATION. BOTH, ANION AND CATION SIZE STRONGLY AFFECT THE MELTING POINT, DECREASING WITH INCREASING ION SIZE. SYMMETRY OF CATIONS WAS FOUND TO ALSO PLAY A CRUCIAL ROLE FOR THE POSITION OF THE MELTING POINT. HIGH SYMMETRY ALLOWS MORE EFFICIENT ION-ION PACKING IN THE CRYSTAL CELL, LEADING TO HIGHER MELTING POINTS WHEREFORE SYMMETRIC CATIONS ARE CONSIDERED LESS FAVORABLE. SUBSTITUENT ALKYL CHAINS LOWER THE MELTING POINT WITH INCREASING LENGTH UP TO APPROXIMATELY C10 WHEN VAN DER WAALS INTERACTIONS BETWEEN THE CHAINS GAIN STRENGTH AND LEAD TO AN INVERSE EFFECT. BRANCHING WAS ALSO FOUND TO NEGATIVELY AFFECT THE MELTING POINT. GENERALLY, ANION VARIATION IS CONSIDERED LESS POTENT FOR MELTING POINT ADJUSTMENT THAN ALTERATION OF THE CATION.

THE UPPER LIMIT OF THE LIQUIDUS RANGE IS SET WITH THE DECOMPOSITION TEMPERATURE OF THE RESPECTIVE ION-ION COMBINATION MOSTLY BETWEEN 350-450°C. IONIC LIQUIDS WERE FOUND TO HAVE A NEGLIGIBLE VAPOR PRESSURE WHICH IS ONE OF THE MOST IMPORTANT ATTRIBUTES FOR THEIR CLASSIFICATION AS GREEN SOLVENTS, RENDERING THEM SUPERIOR OVER COMMON ORGANIC SOLVENTS. THE LOGICAL INITIAL CONCLUSION THEREFORE WAS THAT IF THE VAPOR PRESSURES ARE TOO LOW TO BE DETECTED, DISTILLATION IS NOT POSSIBLE. THIS ASSUMPTION WAS ONE OF THE FIRST DRAWBACKS IN

IONIC LIQUIDS RESEARCH AS IT BECAME INCREASINGLY CLEAR THAT PURIFICATION MAY BECOME A MAJOR PROBLEM FOR MANY CONCEIVED POTENTIAL APPLICATIONS, ESPECIALLY ON A LARGE SCALE. IN 2006, THE GROUP AROUND MARTYN J. EARLE FROM THE QUILL CENTRE IN BELFAST CLAIMED SUCCESSFUL DISTILLATION OF MANY IONIC LIQUIDS WITHOUT DECOMPOSITION AT LOW PRESSURES AND TEMPERATURES BETWEEN 200-300°C [EARLE ET AL. 2006]. TO THEIR DISADVANTAGE, THEY DID NOT PROVIDE ANY PROOF OF THE PRESENCE OF IONS IN THE GAS PHASE KEEPING THE COMMUNITY SUSPICIOUS ABOUT THEIR ACHIEVEMENT [WASSERSCHEID 2006]. APPROXIMATELY ONE YEAR LATER, ARMSTRONG ET AL. PRESENTED DETAILED INFORMATION ABOUT IONIC LIQUID VAPORS BY PROVIDING MASS SPECTROMETRY DATA IDENTIFYING THE GASEOUS PHASE TO PURELY CONSIST OF ION PAIRS [2007]. THE GOOD COMPLIANCE OF THESE RESULTS WITH PREVIOUS VAPOR-PRESSURE MEASUREMENTS PROOFED THE ACCURACY OF THE RESULTS OF EARLE ET AL. AND HENCE THE POSSIBILITY TO DISTILL IONIC LIQUIDS. IN 2010, TAYLOR ET AL. REPORTED THE FRACTIONAL DISTILLATION OF IONIC LIQUID MIXTURES EVEN ALLOWING NOT ONLY TO PURIFY IONIC LIQUIDS BUT ALSO TO SEPARATE IONIC LIQUID MIXTURES SUPPOSING SUFFICIENTLY DIFFERENT VOLATILITY.

RHEOLOGICAL PROPERTIES

THE TRANSPORT PROPERTY CHARACTERIZATION OF IONIC LIQUIDS SUCH AS VISCOSITY, DENSITY AND SURFACE TENSION IS ELEMENTAL TO UNDERSTAND THEIR KINETICS IN CHEMICAL REACTIONS AND TO CONSIDER THEM FOR INDUSTRIAL APPLICATIONS. AS A FIRST CLASSIFICATION, IONIC LIQUIDS ARE CONSIDERED TO BE NEWTONIAN FLUIDS SHOWING A CONSTANT VISCOSITY INDEPENDENT OF STRAIN RATE [MANTZ AND TRULOVE 2003]. NON-NEWTONIAN BEHAVIOUR HASN'T BEEN OBSERVED SO FAR, POTENTIALLY A CONSEQUENCE OF UNAVAILABLE STUDIES SPECIFICALLY FOCUSING ON THIS FEATURE. WITH REGARD TO VISCOSITY, IONIC LIQUIDS ARE GENERALLY KNOWN TO BE RATHER VISCOUS FLUIDS WITH A MINIMUM AT LEAST TWENTY TIMES THE VISCOSITY OF WATER [MACFARLANE ET AL. 2001]. DUE TO AN INFINITE NUMBER OF POSSIBLE ION-ION COMBINATIONS, ALSO THESE VALUES VARY OVER A WIDE RANGE BUT CAN BE FOUND TYPICALLY BETWEEN 21CP AND 500CP. IN COMPARISON, COMMON SOLVENTS LIKE WATER (0.890CP), ETHYLENE GLYCOL (16.1CP) AND GLYCEROL (934CP) GIVE AN IMPRESSION OF WHAT ONE CAN EXPECT WHEN HANDLING IONIC LIQUIDS.

VISCOSITIES WERE FOUND TO BE STRONGLY DEPENDENT ON TEMPERATURE BUT EVEN MORE ON PURITY WHICH IS CONSIDERED BEING THE BIGGEST PITFALL WITH DATA CURRENTLY AVAILABLE IN LITERATURE. AS WITH MOST OTHER FLUIDS, VISCOSITY DECREASES WITH INCREASING TEMPERATURE SOMETIMES TO A FORMIDABLE EXTEND. E.G. BAKER ET AL. FOUND A 27 PERCENT DECREASE IN VISCOSITY BY RAISING THE TEMPERATURE OF 1-BUTYL-3-METHYLIMIDAZOLIUM HEXAFLUOROPHOSPHATE BY ONLY FIVE DEGREES FROM 293°K TO 298°K [2001]. DEVIATIONS OF VALUES ARISING FROM

IMPURITIES E.G. REMAINING CHLORIDE IONS FROM ANION METATHESIS REACTIONS OR WATER WERE FOUND TO BE EXORBITANTLY HIGH. A WATER CONTENT OF ONLY 2 wt% CAN ALTER THE VALUES FOUND FOR IONIC LIQUID VISCOSITY BY UP TO 50 PERCENT AND HALIDE IMPURITIES UP TO ASTONISHING 600 PERCENT [SEDDON ET AL. 2000]. INFLUENCES OF ANION AND CATION SIZE AND CHEMISTRY ON THE VISCOSITY OF IONIC LIQUIDS ARE EXPECTED BUT NOT PROOFED. INCONSTANCIES IN THE DATA AND UNCERTAINTY ABOUT THE PURITY OF THE ANALYZED SAMPLES DO NOT ALLOW MAKING CLEAR PREDICTIONS IN THIS DIRECTION.

DENSITIES OF IONIC LIQUIDS ARE ALSO TEMPERATURE DEPENDENT BUT SIGNIFICANTLY LESS THAN RESPECTIVE VISCOSITIES. TYPICAL VALUES FALL BETWEEN RANGES OF 1.1 – 2.4 g $\cdot$ cm^{-3} LINEARLY DECREASING WITH TEMPERATURE [MANTZ AND TRULOVE 2003]. APPETECCHI ET AL. DETERMINED A DENSITY REDUCTION OF 0.65 g $\cdot$ cm^{-3} FOR THE IONIC LIQUID N-ETHYL-N-METHYLIMIDAZOLIUM BIS(TRIFLUOROMETHANESULFONYL)IMIDE WHEN RAISING THE TEMPERATURE FROM 20°C TO 90°C HENCE 0.01 g $\cdot$ cm^{-3} /°C [2011]. IMPURITIES TEND TO HAVE LESS IMPACT ON THE DENSITY VALUES OF IONIC LIQUIDS AS THEY HAVE ON VISCOSITY. THE AUTHORS ALSO REPORTED ION PACKING AS A PARAMETER CONSIDERABLY INFLUENCING THE DENSITY OF IONIC LIQUIDS. A DECREASE IN DENSITY WAS OBSERVED FOR INCREASING SIDE CHAIN LENGTH OF THE IMIDAZOLIUM CATION WHEREAS ANIONS CAUSE AN INCREASE WHEN THEY BECOME MORE BULKY. THIS WAS ALSO REPORTED BY MANTZ AND TRULOVE [2003].

SURFACE TENSION AS THE RESISTANCE AGAINST AN EXTERNAL FORCE IS ANOTHER IMPORTANT PARAMETER IN CONTEXT OF RHEOLOGICAL PROPERTIES. COMPARABLE WITH IONIC LIQUID DENSITIES, THESE VALUES WERE FOUND TO BE SLIGHTLY DEPENDENT ON TEMPERATURE SLOWLY DECREASING WITH INCREASING TEMPERATURE AND WATER CONTENT [RESTOLHO ET AL. 2009]. SURPRISINGLY, AFTER REACHING A CERTAIN LEVEL IN WATER CONTENT, THE SURFACE TENSION STARTS TO RE-INCREASE. THIS CAN BE EXPLAINED WITH THE DECREASE IN ELECTROSTATIC INTERACTIONS AMONG HYDRATED IONS, WHEN SMALL AMOUNTS OF WATER ARE PRESENT. HYDROGEN BONDS WITH BOTH, CATIONS AND ANIONS, CAUSE A REDUCTION IN THE OVERALL COHESIVE ENERGY AS A CONSEQUENCE OF FORCED MOLECULAR REARRANGEMENT [FREIRE ET AL. 2007]. AT A CERTAIN WATER CONCENTRATION, THIS PROCESS IS FOLLOWED BY COMPLETE SOLVATION OF THE IONIC LIQUID IONS AND PRESENCE OF WATER MOLECULES UNASSOCIATED WITH THEM. THE ANEW TRIGGERED STRUCTURAL REARRANGEMENT NOW RESULTS IN HIGHER SURFACE TENSIONS AS A CONSEQUENCE OF THE GENERALLY HIGHER SURFACE TENSION FOR WATER COMPARED TO IONIC LIQUIDS. THE AUTHORS ADDITIONALLY INJECTED THAT THIS EFFECT IS TYPICAL FOR HYDROPHILIC IONIC LIQUIDS AND LESS LIKELY TO BE OBSERVED FOR THEIR RATHER HYDROPHOBIC COUNTERPARTS WHERE SIMILAR VALUES CAN BE MEASURED IN WET AND DRY STATE.

POLARITY

SOLVENT POLARITY IS CONSIDERED AS ONE OF THE MOST IMPORTANT SOLVENT PARAMETERS DESCRIBING THE GLOBAL SOLVATION CAPABILITY. THIS RATHER COMPLEX SOLVENT CHARACTERISTIC OCCURS AS A CONSEQUENCE OF A MULTI-LAYERED INTERPLAY OF MOLECULAR INTERACTIONS OFTEN DECLARED AS THE STATIC DIELECTRIC CONSTANT ε_S. VALUES FOR THIS SOLVENT PARAMETER ARE AVAILABLE FOR MOST MOLECULAR LIQUIDS BUT ARE DIFFICULT TO DETERMINE FOR IONIC LIQUIDS DUE TO THEIR CONDUCTIVITY. DIRECT MEASUREMENT IS USUALLY RESTRICTED TO NON-CONTACTING MEDIUMS WHEREFORE DIELECTRIC CONSTANT VALUES ARE NOT DIRECTLY ACCESSIBLE FOR IONIC LIQUIDS. INDIRECT DETERMINATION IS POSSIBLE BY MEASURING THE FREQUENCY DEPENDENT DIELECTRIC PERMITTIVITY AND EXTRAPOLATION TO ZERO FREQUENCY, CLASSIFYING IONIC LIQUIDS AS SOLVENTS OF MODERATE POLARITY PARTICULARLY IF DIPOLAR CATIONS ARE THE COUNTERPART TO LOW DIPOLE MOMENT ANIONS E.G. TETRAFLUOROBORATE AND HEXAFLUOROPHOSPHATE [WEINGÄRTNER 2008]. A SHIFT TO HIGHER DIELECTRIC CONSTANT VALUES FOR A GIVEN CATION CAN BE ACHIEVED BY COMBINATION WITH ANIONS EXHIBITING HIGH DIPOLE MOMENTS I.E. ALKYLSULFATES. THE ARDUOUS ACCESSIBILITY AND THE LARGELY INCOMPARABLENESS WITH MANY EXPERIMENTAL DATA LED TO THE DEVELOPMENT AND USE OF EMPIRICAL METHODS TO DESCRIBE IONIC LIQUID POLARITY [CROWHURST ET AL. 2003].

A PROMINENT EMPIRICAL METHOD FOR DETERMINING THE POLARITY OF AN IONIC LIQUID SOLVENT IS THE UTILIZATION OF THE KAMLET-TAFT PARAMETERS, DEVELOPED AND INTRODUCED BY KAMLET AND TAFT [1976]. THIS SYSTEM IS BASED ON COMPARISON OF CLOSELY RELATED DYES ACCORDING TO THEIR UV-VIS SPECTRA. THE ABSORPTION BANDS OF THESE DYES FORM THE BASIS FOR THE SCALES OF HYDROGEN BOND ACIDITY (α), HYDROGEN BOND BASICITY (β) AND DIPOLARITY/POLARIZABILITY EFFECTS (π^*) AS A SUITABLE SET OF PARAMETERS TO DESCRIBE THE POLARITY OF A SOLVENT INDEPENDENT OF CONDUCTIVITY. THIS SET OF DYES IS SHOWN IN **FIGURE 12**.
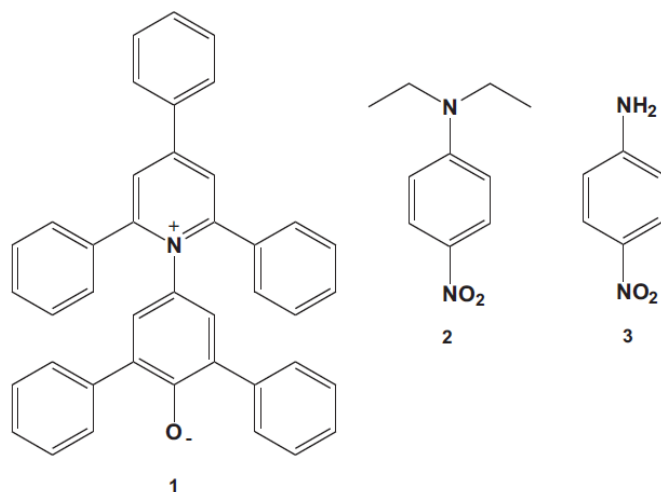

FIGURE 12. *REICHARDT'S DYE (1), N,N-DIETHYL-4-NITROANILINE (2) AND 4-NITROANILINE (3)*

The hydrogen-bond acidity **α** of a solvent is determined by analyzing the longest-wavelength absorption band shift of Reichardt's dye (**1**), showing one of the largest known solvatochromic shifts [Reichardt 1992; Welton 2003]. It's ability to register effects originating from solvent dipolarity, hydrogen bonding, Lewis acidity and in particular contributions through the hydrogen bond donor property of a solvent, renders it as suitable indicator for **α**. The nature of the cation was found to have the strongest impact on its values but anions can have an influence too. With increasing basicity of the anion, the hydrogen-bond donor ability of the respective ionic liquid decreases although the cation remains unchanged. Crowhurst et al. explains this finding either with a competition between the anion and the probe dye solute for the proton or a direct interaction between anion and dye [2003].

β indicates the hydrogen bond basicity and is determined by the band shift of 4-nitroanailine (**3**). These values are prevailingly dependent on the anion but the nature of the cation can act as a modulator. These values are an indicator for the interaction with the solute species and can eventually be used as predictors for solvency power of the ionic liquid towards certain solutes [Doherty et al. 2010].

The third parameter **π*** indicates the dipolarity and polarizability of a solvent by interaction of the local electric fields of the ionic liquid and the dye *N,N*-diethyl-4-nitroaniline (**2**) causing an change of the absorption maximum. Both cations and anions can affect this value to a very limited extend. Increasing delocalization of the anion charge causes a decrease in **π***, whereas charge delocalization in cations e.g. around the imidazolium ring in imidazolium-type ionic liquid leads to an increased polarizability and hence higher **π*** values. **Figure 13** gives an overview about the individual interactions of the ionic liquid 1-butyl-3-methylimidazolium chloride with this set of dyes.
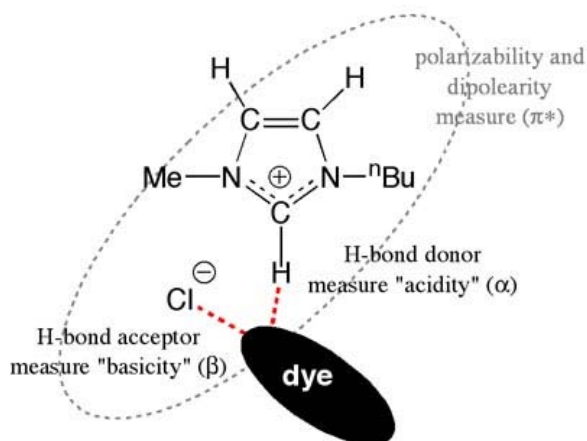

*Figure 13. Kamlet Taft parameters **α**, **β** and **π*** as indicators for ionic liquid-dye interactions [Hunt research group. Imperial College London]*

IONIC LIQUIDS ARE FOUND TO BE MODERATELY POLAR SOLVENTS COMING IN THE RANGE OF ACETONITRILE, DMSO OR SHORT- TO MEDIUM-CHAIN ALCOHOLS. GENERALLY THEY CAN ACT AS BOTH, HYDROGEN BOND ACIDS AND/OR HYDROGEN BOND BASES, OR AS NEITHER [WELTON 2003]. MOST IMPORTANTLY, THESE FEATURES CAN BE STEERED WITHIN LIMITS BY SELECTION OF SUITABLE CATION-ANION COMBINATIONS. HYDROGEN BOND BASICITY CAN BE ADJUSTED BY CHOICE OF THE ANION AND HYDROGEN BOND ACIDITY WITH SELECTION OF THE CATION RESPECTIVELY. NONE OF THEM WERE FOUND TO BE SUPER-POLAR AND NO SUCH THING AS AN IONIC LIQUID EFFECT COULD BE OBSERVED SO FAR. THE HIGH IMPACT OF SOLVENT POLARITY ON CHEMICAL REACTIONS AND THE OPPORTUNITIES ARISING FROM THE ADJUSTABILITY OF THIS PARAMETER WITHIN IONIC LIQUIDS RENDER THESE INVESTIGATIONS OF HIGH IMPORTANCE BUT UNFORTUNATELY ALSO VERY LABORIOUS DUE TO AN ALMOST INFINITE NUMBER OF POSSIBLE ION-ION COMBINATIONS WAITING TO BE CHARACTERIZED.

2. PROJECTS

2.1 ORGANOSOLV-BASED BIOREFINERY

DUE TO FADING FOSSIL RESOURCES, VALORIZATION OF RENEWABLE RESOURCES IS ON THE RISE [CLARK ET AL. 2006]. THE ENORMOUS DEMAND FOR ENERGY CURRENTLY COVERED THROUGH PETROLEUM REFINERY IS THE MAIN DRIVING FORCE BEHIND THIS PROCESS. THE ONGOING CHANGE TO INEXHAUSTIBLE ENERGY SOURCES DOES NOT ONLY REQUIRE NEW TECHNOLOGIES FOR BIOMASS PROCESSING BUT WILL ALSO LEAD TO NEW INDUSTRY BRANCHES FOR PLATFORM CHEMICALS. BIOCONVERSION OF RENEWABLE RESOURCES BY TREATMENT WITH HOT AQUEOUS ETHANOL, KNOWN AS THE ORGANOSOLV PROCESS, IS AN OLD CONCEPT DATING BACK TO 1931 [KLEINERT AND TAYENTHAL]. ALTHOUGH THE IDEA OF SEPARATING OR EXTRACTING COMPONENTS OUT OF WOODEN MATERIALS AROSE ALREADY IN THE EARLY 19TH CENTURY, THE MIDDLE OF THE 20TH CENTURY CAN BE CONSIDERED AS THE TIME, WHEN THIS CONCEPT DREW ATTENTION TO A LARGER COMMUNITY. WITH THE BEGINNING OF THE 1980S, THE INTEREST IN THIS RESEARCH AREA INCREASED REMARKABLY. ORGANOSOLV PULPING AS A CONCEIVABLE "GREEN", SULFUR-FREE ALTERNATIVE TO ESTABLISHED SULFUR-CONTAINING PULPING PROCESSES SUCH AS KRAFT OR SULFITE WAS THE MAIN DRIVING FORCE AND GAINED WIDESPREAD INTEREST WITH ITS PEAK IN THE NINETIES. WITH THE ESTABLISHMENT AS A PROMISING APPROACH FOR THE FUTURE, NEW POSSIBLE FACETS APPEARED IN SCIENTIFIC DATABASES. THE NEW FOCUS WAS DIRECTED TO OTHER POSSIBLE RENEWABLE MATERIALS FOR ORGANOSOLV PROCESSING SUCH AS STRAW AND ANNUAL PLANTS. THE LATEST DEVELOPMENT IN THIS SCIENTIFIC AREA IS THE USE OF ORGANOSOLV PRINCIPLES AS A PRETREATMENT STEP PREVAILINGLY IN BIOETHANOL PRODUCTION. HIGH ACHIEVABLE DELIGNIFICATION RATES INCREASE THE ENZYMATIC CONVERSION RATE AND HENCE THE OVERALL BIOETHANOL OUTPUT FROM LIGNOCELLULOSIC MATERIALS [PAN ET AL. 2006]. CONSIDERABLE PRETREATMENT EFFECTS CAN ALSO BE OBTAINED BY SIMPLY USING HOT WATER INSTEAD OF AN ALCOHOL/WATER MIXTURE BUT THIS ALLOWS ONLY SIGNIFICANTLY LOWER DELIGNIFICATION RATES [ZENG ET AL. 2007; ÖHGREN ET AL. 2007].

ORGANOSOLV CONDITIONS USUALLY INVOLVE A MIXTURE OF WATER AND AN ALIPHATIC ALCOHOL, MAINLY ETHANOL, IN VARIOUS RATIOS [MUURINEN 2000]. COMPARABLE RESULTS CAN ALSO BE ACHIEVED BY USING METHANOL [OLIET ET AL. 2002]. THIS SOLVENT COMBINATION IS KNOWN AS THE ORGANOCELL CONCEPT. AN OVERVIEW ABOUT MOST PROMINENT CONCEPTS UTILIZING ORGANIC CHEMICALS IS GIVEN IN **FIGURE 14**.
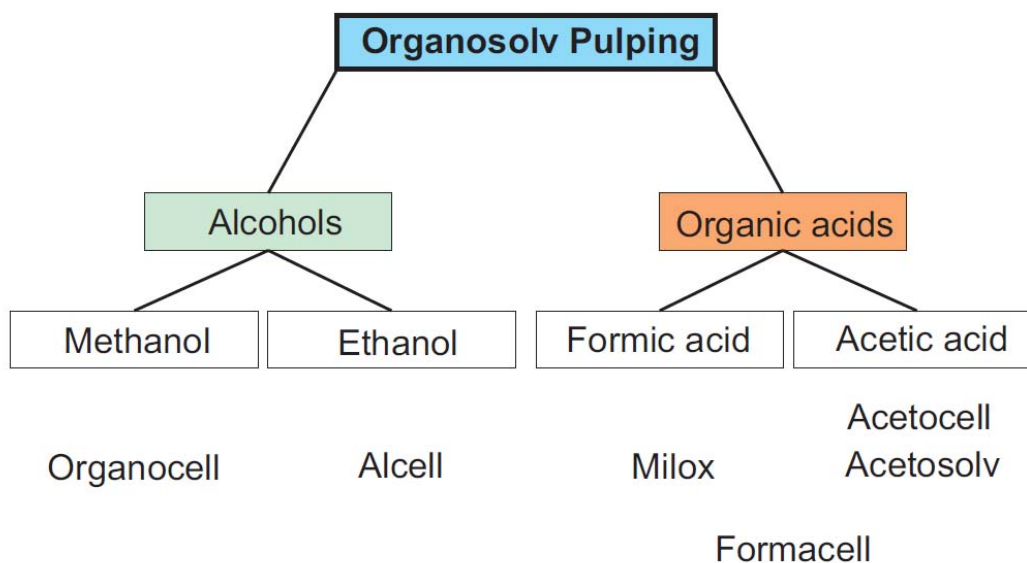
FIGURE 14. *OVERVIEW ABOUT PROMINENT ORGANOSOLV CONCEPTS/PROCESSES*

SUPERCRITICAL CARBON DIOXIDE AS A CO-SOLVENT CAUSES AN ANOMALOUS POROSITY AND LAMELLAR STRUCTURE WITHIN THE MATERIAL RESULTING IN A HIGHER ACCESSIBILITY FOR THE ETHANOL-WATER MIXTURE [GAO ET AL. 2010; PASQUINI ET AL. 2005]. THE SIGNIFICANTLY HIGHER SOLUBILITY OF CARBON DIOXIDE IN ETHANOL IN OPPOSITE TO WATER MAKES THE APPLICATION OF AN ALCOHOL WATER MIXTURE EVEN MORE PREFERABLE OVER PURE WATER PRETREATMENT [DALMOLIN ET AL. 2006]. PRETREATMENT STEPS WITH SIMILAR GASES SUCH AS SULFUR DIOXIDE ARE ALSO CAPABLE TO ENHANCE THE DELIGNIFICATION AND ADDITIONALLY AT CONCEIVABLE LOWER TEMPERATURES AND PRESSURES [SASSNER ET AL. 2005]. THE MAJOR DRAWBACK OF SULFUR DIOXIDE COMES FROM THE CHEMICAL MODIFICATION OF THE LIGNIN – UTILIZATION OF SULFUR DIOXIDE TYPICALLY LEADS TO FORMATION OF LIGNOSULFONATES. THE EVERLASTING ISSUE IN ENERGY PRODUCTION BASED ON RENEWABLE MATERIALS IS HOW TO MAKE SUCH A PROCESS PROFITABLE. RESOURCES LIKE STRAW ARE CHEAP BUT THE ENERGY INPUT FOR TRANSFORMATION INTO BIOETHANOL OR BIOGAS IS COMPARABLY HIGH, RENDERING A SIMPLE CONVERSION BARELY FEASIBLE. AS PULP RESULTING FROM ORGANOSOLV TREATMENT OF STRAW AND OTHER ANNUAL PLANTS DOES NOT SHOW SUFFICIENT QUALITY TO ENTER THE PAPER AND FIBER INDUSTRY, OTHER MAIN CONSTITUENTS NEED TO BE TRANSFORMED INTO VALUE-ADDED PRODUCTS TO SUSTAIN SUCH A CONCEPT. LIGNIN, ONE OF THE MAIN COMPONENTS IN ALL NATURALLY GROWN MATERIALS, SHOWS A HIGH POTENTIAL TO MEET THIS DEMAND ALTHOUGH EFFICIENT USAGE COULD NOT BE ESTABLISHED IN THE PAST. UNTIL NOW, RATHER NEGLECTED BY SIMPLY USING IT AS FUEL, VARIOUS MORE BENEFICIAL APPLICATIONS ARE CONCEIVABLE. THE USAGE OF ORGANOSOLV LIGNIN AS A POLYPHENOL SOURCE IS JUST ONE ECONOMICALLY INTERESTING ALTERNATIVE, PROVIDED PURE ISOLATION. LIGNOSULFONATES REPRESENT ANOTHER OPPORTUNITY FOR LIGNIN VALORIZATION WITH A LARGE VARIETY OF APPLICATIONS.

A VERY PROMISING APPLICATION IS THE USE OF ORGANOSOLV LIGNIN AS A SOURCE FOR ARTIFICIAL HUMIC SUBSTANCES WHICH CAN BE APPLIED FOR RECULTIVATION OF DEGRADED SOILS OR GENERAL SOIL IMPROVEMENT. PROGRESSIVE DESERTIFICATION IN PARTS OF THE WORLD RENDERS THIS PRODUCT CLASS HIGHLY BENEFICIAL IN THE FUTURE. AMMONOXIDATION IS ONE OF THE TECHNOLOGICAL OPPORTUNITIES FOR CONVERTING LIGNIN AND OTHER LIGNEOUS BIOMATERIALS INTO NITROGEN-RICH ORGANO-MINERAL SOIL IMPROVERS THAT SHARE A COUPLE OF SIMILARITIES WITH NATURAL HUMIC SUBSTANCES [LIEBNER ET AL. 2006]. THE SPECIAL VALUE OF THESE MODIFIED LIGNINS IS THE SLOW RELEASE OF NITROGEN DUE TO DIFFERENT BINDING FORMS OF NITROGEN GENERATED UPON AMMONOXIDATION. THE FACT, THAT SUBSTANTIALLY DELIGNIFIED RENEWABLE MATERIALS ARE IN ADDITION MUCH EASIER CONVERTED TO DEGRADATION PRODUCTS SUCH AS BIOETHANOL OR BIOGAS, SERVED AS SOURCE OF INSPIRATION IN THE DEVELOPMENT OF AN ORGANOSOLV-BASED BIOCONVERSION PROCESS MAXIMIZING THE ISOLATED AMOUNT OF PURE LIGNIN.

2.1.1 PROCESS DEVELOPMENT

THE AIM OF THIS PROJECT WAS TO VERIFY THE FEASIBILITY OF A NEW BIOREFINERY CONCEPT UTILIZING CHEAP RENEWABLE RESOURCES. TO OVERCOME HIGH PROCESS ENERGY DEMANDS IN THE PRODUCTION OF LOW-VALUE BULK PRODUCTS LIKE BIOETHANOL OR BIOGAS, LIGNIN AS A SOURCE FOR ARTIFICIAL HUMIC SUBSTANCES WAS CONSIDERED AS A VALUABLE BY-PRODUCT THAT COULD FULFILL THE REQUIREMENTS FOR AN ECONOMICALLY FEASIBLE PROCESS. THE DEVELOPED PROCESS, CLASSIFIED ACCORDING THE IEA BIOENERGY TASK 42, CAN BE DESCRIBED AS FOLLOWS:

PROCESS CLASSIFICATION: C5/C6 SUGARS AND LIGNIN BIOREFINERY FOR ARTIFICIAL HUMIC SUBSTANCES, BIOETHANOL AND BIOGAS FROM LIGNOCELLULOSIC RESIDUES (STRAW)

PLATFORMS: LIGNIN (N-MODIFIED), C5/C6 SUGARS, (PULP)
PRODUCTS: ARTIFICIAL HUMIC SUBSTANCES, BIOETHANOL, BIOGAS
FEEDSTOCK: LIGNOCELLULOSIC RESIDUES (STRAW)
CONVERSION PROCESSES: MECHANICAL, THERMO-CHEMICAL

A SCHEMATIC OVERVIEW OF THE PRESENTED PROCESS IS GIVEN IN **FIGURE 15**:
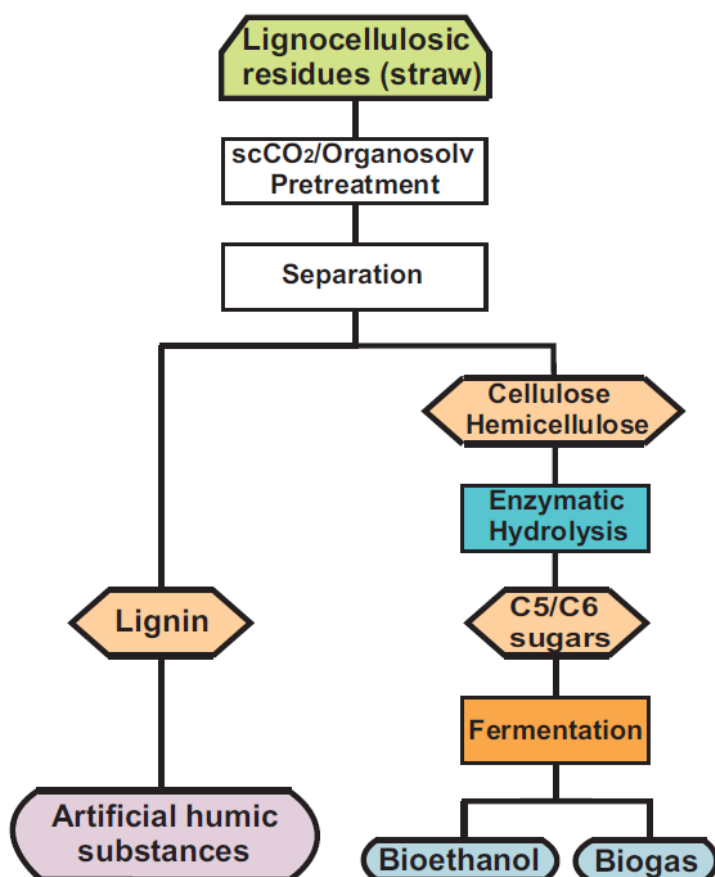

FIGURE 15. BIOREFINERY – PROCESS CLASSIFICATION

This study reinvestigated the well known Organosolv concept aiming at maximum lignin output using scCO$_2$ as co-solvent. Lignin is a still underestimated natural resource with potential applications in the near future. The use of *N*-modified lignins as soil improvers was considered being one of the most interesting utilizations in response to progressive desertification in parts of the world. The presented process uses rye straw as a renewable source achieving up to seventy percent delignification with lignin purities of 80-85% and nitrogen contents of up to four percent. The nitrogen enrichment was achieved by thermal treatment of rye straw under alkaline Organosolv conditions simultaneously using aqueous NH$_4$OH as nitrogen source and supercritical carbon dioxide as pulping additive. The effectiveness of scCO$_2$ as co-solvent could be demonstrated in a model substance study, which will be presented in chapter 2.1.2.

The work conducted within this thesis was focused on the pretreatment, separation and characterization of the obtained fractions. The right branch of the flow chart (**Figure 15**) has been and will be further investigated by cooperation partners.

Experimental

Chemicals

Chemicals were obtained from commercial sources and were of the highest purity available. Rye straw was obtained from different suppliers in Lower Austria and milled to <1 mm containing and average water content of 6.3%.

Experimental setup

The CO$_2$ assisted Organosolv pulping was performed in a 0.2 l autoclave with jacketed heater (Separex, France). 12 g of rye straw were mixed with 100 ml 50% (v/v) ethanol in water (<u>initial phase</u>) or aqueous ammonium hydroxide (0.1, 2.5, 5.0, 10.0 wt.-% NH$_3$) and equilibrated for 15 min. After equilibration, the mixture was filled into the preheated autoclave (80°C) and pressurized with CO$_2$ to 6 MPa. Subsequently, the heating jacket was heated to the desired temperature (150-180°C). After reaching the adjusted value, the system was pressurized (6-16 MPa) using a hand-piston-pump (Sitec, Switzerland) and left under these conditions until the individual reaction time had elapsed (10-160 min). After the treatment, the system was depressurized and the solid residue was washed with 400 ml 0.1 N NaOH and filtered off. The residue was enriched cellulose whereas the supernatant mainly contained lignin and hemicellulose. In order to separate these fractions, the supernatant was acidified with

HYDROCHLORIC ACID TO A pH BELOW 3, LEADING TO PRECIPITATION OF THE LIGNIN. AFTER FILTRATION, THE TWO SOLID FRACTIONS WHERE DRIED AT 70°C, WEIGHED AND, TOGETHER WITH THE SUPERNATANT, SUBJECTED TO FURTHER ANALYSIS.

GENERAL ANALYTICS

GPC SYSTEM: FOR GPC MEASUREMENTS, THE SYSTEM AS DESCRIBED BY RÖHRLING ET AL. WAS USED [2002]: ONLINE DEGASSER, DIONEX DG-2410, KONTRON 420 PUMP; PULSE DAMPER; AUTOSAMPLER, HP SERIES 1090; COLUMN OVEN, REFRACTIVE INDEX (RI) DETECTOR, SHODEX RI-101. DMAc/LiCl (0.9%, W/V), FILTERED THROUGH A 0.02 µm FILTER, WAS USED AS THE ELUANT. THE SAMPLE WAS INJECTED AUTOMATICALLY, CHROMATOGRAPHED ON TWO SERIAL GPC COLUMNS, AND MONITORED BY RI DETECTION. MOLECULAR WEIGHT DISTRIBUTION AND RELATED POLYMER RELEVANT PARAMETERS WERE CALCULATED BY SOFTWARE PROGRAMS. THE FOLLOWING PARAMETERS WERE USED IN THE GPC MEASUREMENTS: FLOW, 1.00 ml $\cdot$ min^{-1}; COLUMNS, TWO, PL GEL MIXED A LS, 20 µm, 7.5x300 mm; INJECTION VOLUME: 100µl; RUN TIME, 45 min. DATA EVALUATION FOR LIGNIN MOLECULAR WEIGHT ARE BASED ON CALIBRATION WITH NARROW POLYSTYRENE STANDARDS (ASTRA 5 SOFTWARE). STANDARDS USED FOR CALIBRATION: 30 kg $\cdot$ mol^{-1}, 114.2 kg $\cdot$ mol^{-1}, 200 kg $\cdot$ mol^{-1}, 300 kg $\cdot$ mol^{-1}, 700 kg $\cdot$ mol^{-1}.

CURIE-POINT PYROLYSIS GC/MS: WAS PERFORMED USING A CPP-40 PYROLYSER (GSG) COUPLED WITH A GC 6890 AND MSD 5973 (AGILENT TECHNOLOGIES). 260 µg OF THE SAMPLE WAS PYROLYSED AT 600°C (FECRALLOY^{TM}) FOR 10 SECONDS. THE PYROLYSATE WAS CARRIED BY HELIUM INTO THE INLET (250°C, SPLIT 1:20) OF THE GAS CHROMATOGRAPH. SEPARATION WAS ACHIEVED USING A FUSED SILICA HP-5ms COLUMN (30 m, 0.25 mm, 25 µm) AND A COLUMN FLOW OF 1.0 ml $\cdot$ min^{-1}. OVEN PROGRAM: 50°C (5 min), 5°C $\cdot$ min^{-1} TO 180°C, THEN 10°C $\cdot$ min^{-1} TO 280°C (9 min). AUXILIARY TEMPERATURE: 250°C (18 min), 10°C $\cdot$ min^{-1} TO 280°C (14 min). MASS SPECTROMETER: EI MODE (70 eV); ION SOURCE 230°C; QUADRUPOLE 150°C, 7.6 $\cdot$ 10^{-6} Torr. PEAK ASSIGNMENT WAS ACCOMPLISHED USING THE NIST 2005 MASS SPECTRA DATABASE.

ELEMENTAL ANALYSIS (C, H, N): WAS PERFORMED AT THE MICROANALYTICAL LABORATORY OF THE UNIVERSITY OF VIENNA.

ANALYSIS OF ASH AND MINERALS: WAS PERFORMED BY THE INSTITUTE OF WASTE MANAGEMENT AT THE UNIVERSITY OF NATURAL RESOURCES AND LIFE SCIENCES, VIENNA. SAMPLES WERE HEATED UP IN ALUMINUM OXIDE CRUCIBLES TO 950°C WITH A RATE OF 10K $\cdot$ min^{-1}, GAS FLOW 150 ml $\cdot$ min^{-1} (80%He/20%O$_2$) USING 16 mg MATERIAL PER ANALYSIS.

STATISTICS

STATISTICAL EXPERIMENTAL DESIGN WAS DONE WITH CADEMO (COMPUTER AIDED DESIGN OF EXPERIMENTS AND MODELING) FROM BIOMATH GMBH USING A BOX-BEHNKEN DESIGN. DESIGN AND CALCULATION WERE DONE BY THE DEPARTMENT OF APPLIED STATISTICS AT THE UNIVERSITY OF NATURAL RESOURCES AND LIFE SCIENCES, VIENNA.

RESULTS AND DISCUSSION

IN THE <u>INITIAL PHASE</u> OF THE PROJECT, VARIOUS CHEMICALS, E.G. ACIDS AND BASES, HAVE BEEN TESTED AS PULPING ADDITIVES TO POTENTIALLY RAISE THE LIGNIN OUTPUT AND OR AFFECT ITS PURITY. ALTERATIONS IN THE CONSUMPTION OF THE WASHING SOLUTIONS WERE CONDUCTED FOR THE SAME PURPOSE. AFTER THIS PHASE, A STATISTICAL APPROACH WAS USED TO FIND OPTIMAL VALUES FOR DECISIVE PROCESS PARAMETERS (T, p, t, $c_{Ammonia}$).

THE ORGANOSOLV PULPING PROCESS IS KNOWN TO WORK BEST WITH EQUIVALENT ALCOHOL WATER RATIOS AT TEMPERATURES SLIGHTLY ABOVE 180°C WHEN HIGH LIGNIN OUTPUT IS DESIRED. THE REACTION TIME APPEARS TO BE DIRECTLY PROPORTIONAL TO THE YIELD LEADING TO INCREASING YIELDS WITH INCREASING TIME [<u>PAN ET AL. 2006</u>]. WITH THIS KNOWLEDGE, THE TEST PARAMETERS FOR THE INITIAL PHASE WERE CHOSEN TO BE 180°C, 16 MPa AND 160 min. THE RATHER HIGH PRESSURE IS DUE TO SEVERAL FACTORS. FIRST, CARBON DIOXIDE IS KNOWN TO CHANGE INTO THE SUPERCRITICAL STATE AT 31°C AND 7.3 MPa. SECOND, IN COMBINATION WITH THE WATER/ETHANOL MIXTURE, THE REQUIRED PRESSURE TO KEEP THIS TERNARY MIXTURE IN THE LIQUID STATE AT THIS TEMPERATURE IS EVEN HIGHER. IN ADDITION TO THIS, HIGH PRESSURES GUARANTEE A HIGH CONCENTRATION OF CARBON DIOXIDE IN THE ETHANOL-WATER MIXTURE.

THE FIRST TESTS SHOWED THAT ETHANOL GIVES ONLY SLIGHTLY BETTER YIELDS THAN METHANOL WITH COMPARABLE PURITY OF THE OBTAINED LIGNIN FRACTION. AS METHANOL IS APPROXIMATELY TWENTY PERCENT CHEAPER THAN ETHANOL, WE CONTINUED THE STUDY WITH METHANOL AS THE CO-SOLVENT. ADDITION OF ACID (H_2SO_4) GAVE GOOD YIELDS FOR THE LIGNIN BUT VERY LOW YIELDS FOR THE CELLULOSE FRACTION. AS THIS FRACTION IS ALSO RELEVANT FOR THE ECONOMICS OF THIS CONCEPT, THIS ADDITIVE HAS TO BE CONSIDERED UNFAVORABLE. THE ADDITION OF BASE (NaOH) TURNED OUT TO BE SIMILAR UNFAVORABLE AS THIS CAUSED VERY IMPURE LIGNIN FRACTIONS. THE EFFECTIVENESS OF CARBON DIOXIDE WAS PROVEN WITH TWO EXPERIMENTS UNDER ATMOSPHERIC PRESSURE AND AT 16 MPa, USING NITROGEN INSTEAD OF scCO$_2$. THE OBTAINED YIELDS WERE 38% AND 13% LOWER, RESPECTIVELY. THE RESULTS INDICATE THAT THE HIGH PRESSURE ITSELF CAUSES INCREASING YIELDS BUT ONLY CARBON DIOXIDE CAN RAISE THE YIELD EVEN FURTHER. EXPERIMENTS WITH THE WASHING SOLUTION SHOWED THAT IT IS NOT POSSIBLE TO EXTRACT LIGNIN WITH PURE WATER. VERY GOOD RESULTS COULD BE ACHIEVED WITH 1 N NaOH BUT THIS LED TO VERY HIGH SALT CONCENTRATIONS AND IMPURITIES IN THE LIGNIN FRACTIONS. THE USAGE OF 0.1 N NaOH GAVE JUST SIX PERCENT LOWER YIELDS BUT THE SALINITY AND PURITY WERE SIGNIFICANTLY BETTER. 1 N NH$_4$OH ALSO SHOWED SOME POTENTIAL AS WASHING SOLUTION BUT GAVE SIXTY PERCENT LOWER YIELDS RENDERING THIS ALTERNATIVE NOT VERY APPLICABLE. ON THE CONTRARY, USAGE OF AQUEOUS AMMONIUM HYDROXIDE AS REPLACEMENT OF WATER DURING THE PULPING

PROCESS LED NOT ONLY TO GOOD YIELDS BUT ALSO TO NITROGEN ENRICHMENT IN THE LIGNIN FRACTION OF UP TO FOUR PERCENT.

THE NEXT STEP WAS TO FIND THE OPTIMAL OPERATING PARAMETERS FOR THE DESCRIBED PROCESS. FOR THIS PURPOSE, A STATISTICAL APPROACH WAS USED TO REDUCE THE OVERALL NUMBER OF EXPERIMENTS AND TO AVOID SYSTEMATIC ERRORS. THE LIMITS FOR AN EFFECTIVE PROCESS WERE CONSIDERED TO BE BETWEEN 150-180°C WITH A PRESSURE BETWEEN 6-16 MPa, REACTION TIMES OF 10-160 min AND AN AMMONIUM HYDROXIDE CONCENTRATION BETWEEN 0.1 - 10%. **TABLE 4** GIVES AN OVERVIEW ABOUT THESE EXPERIMENTS INCLUDING ACHIEVED YIELDS AND APPROXIMATE PURITY FOR THE CELLULOSE AND THE LIGNIN FRACTIONS.

TABLE 4. STATISTICAL EXPERIMENT DESIGN AFTER BOX-BEHNKEN

	T [°C]	p [bar]	t [min]	NH$_4$OH conc. [%]	Residual cellulosic material [%]	Polysaccharide content pulp [%]	Obtained Lignin [%]	Polysaccharide content lignin [%]
	Block points							
1	157	85	47	2.5	72.3	60.9	1.8	4.7
2	172	85	47	2.5	68.8	60.8	7.7	*n.a.*
3	157	135	47	2.5	75.0	57.5	8.0	*n.a.*
4	172	135	47	2.5	66.1	57.6	4.5	9.0
5	157	85	122	2.5	67.9	55.7	12.5	*n.a.*
6	172	85	122	2.5	59.8	56.7	4.5	12.9
7	157	135	122	2.5	70.5	53.7	2.7	*n.a.*
8	**172**	**135**	**122**	**2.5**	**65.2**	**55.8**	**14.3**	**19.7**
9	157	85	47	7.5	77.7	64.9	8.9	15.8
10	172	85	47	7.5	67.9	64.6	5.4	10.3
11	157	135	47	7.5	59.8	62.4	2.7	8.0
12	172	135	47	7.5	71.4	67.5	11.6	20.3
13	157	85	122	7.5	66.1	72.3	3.6	9.4
14	172	85	122	7.5	72.3	61.3	10.7	11.1
15	157	135	122	7.5	74.1	63.6	9.8	*n.a.*
16	172	135	122	7.5	52.7	*n.a.*	5.4	10.8
	Face points							
17	150	110	85	5.0	62.2	61.6	6.3	9.8
18	180	110	85	5.0	58.9	56.7	7.1	6.8
19	165	60	85	5.0	63.4	57.3	11.6	9.8
20	165	160	85	5.0	59.8	62.0	7.1	*n.a.*
21	165	110	10	5.0	74.1	52.3	3.6	*n.a.*
22	**165**	**110**	**160**	**5.0**	**86.6**	**68.0**	**14.3**	**14.2**
23	165	110	85	0.1	64.3	*n.a.*	8.0	*n.a.*
24	165	110	85	10.0	67.9	55.8	7.1	*n.a.*
	Center point							
25	165	110	85	5.0	67.0	67.6	8.9	*n.a.*

THE BOLD BLACK HIGHLIGHTED TESTS 8 AND 22 IN **TABLE 4** INDICATE THE BEST PULPING CONDITIONS WHEN AIMING FOR MAXIMAL LIGNIN OUTPUT. WITH AN APPROXIMATE STRAW LIGNIN CONTENT OF ABOUT TWENTY PERCENT, BOTH CONDITIONS LEAD TO APPROXIMATELY SEVENTY PERCENT DELIGNIFICATION WITH A LIGNIN PURITY OF 80-85%.

ALL PURITY VALUES HAVE BEEN DETERMINED BY CURIE-POINT PYROLYSIS GC/MS. PURITY EVALUATION IS BASED ON CALIBRATION WITH LIGNIN STANDARDS TO WHICH 2.5, 5.5 AND 10.5 WT.-% OF PULP WERE ADDED. THE EVALUATION OF THE POLYSACCHARIDE CONTENT OF THE ANALYZED SAMPLES WAS DONE BY COMPARING THE PEAKS OF FURFURAL AND GUAIACOL IN THE PYROGRAMS. FURFURAL IS AN INDICATOR FOR THE SUGAR CONTENT WHEREAS GUAIACOL IS THE MAIN FRAGMENT OCCURRING AFTER THERMAL DEGRADATION OF THIS TYPE OF LIGNIN. ANALYSIS OF THE HYDROXYMETHYL-FURFURAL PEAK AS THE MAIN PRODUCT OF HEXOSES SHOWED THAT IT HAS ONLY MINOR EFFECT ON THE OVERALL RESULT AND WAS THEREFORE NOT TAKEN INTO ACCOUNT. WE ARE AWARE OF THE FACT, THAT THIS EVALUATION METHOD IS NOT ENTIRELY CORRECT BUT USEFUL TO GET A ROUGH IDEA OF THE ACHIEVED FRACTION PURITY. FOR THE ANTICIPATED PUBLICATION, EXACT EVALUATION WILL BE DONE AS DESCRIBED BY SCHREMS ET AL. [2011]. THE MOLECULAR WEIGHT OF THE (*N*-MODIFIED) LIGNIN WAS DETERMINED WITH GPC ANALYSIS AND WAS FOUND TO BE RELATIVELY HOMOGENOUS WITH AN AVERAGE OF 7.9 kg · mol^{-1} ± 1.3. ANALYSIS OF THE ASH AND MINERAL CONTENT DISPLAYED A RATHER LOW CONCENTRATION WITHIN THE LIGNIN FRACTION WITH AN AVERAGE ASH CONTENT OF 3.1% ± 1.5.

THESE RESULTS ALSO SHOW THAT THERE IS A STRONG DEPENDENCY TOWARDS ALL REACTION PARAMETERS. DEPENDING ON THE SITUATION IT CAN BE CHOSEN BETWEEN A SHORTER BUT HIGHER ENERGY INPUT OR LONGER LESS INTENSIVE CONDITIONS. WITH AN AVERAGE NITROGEN ENRICHMENT IN THE LIGNIN FRACTION OF 4%, THIS PROCESS CAN BE CONSIDERED AS A PROMISING CONCEPT FOR THE PRODUCTION OF NITROGEN-RICH LIGNINS THE LATTER BEING WORTH TO BECOME SUBJECT OF A THOROUGH STUDY EVALUATING THEIR FERTILIZING AND SOIL IMPROVING EFFECTS AS WELL AS THEIR BIO- AND PHYTOACTIVITY.

CONCLUSION

THE DEVELOPED PROCESS ALLOWS THE ISOLATION OF ABOUT SEVENTY PERCENT OF THE TOTAL LIGNIN CONTENT IN RYE STRAW. SIGNIFICANT INCREASE OF THE LIGNIN OUTPUT CAN BE ACHIEVED BY APPLYING HIGH PRESSURE DURING THE PROCESS. HIGHEST AMOUNTS CAN BE OBTAINED WHEN scCO$_2$ IS USED DURING THE PULPING PROCESS. THIS EFFECT CAN BE EXPLAINED BY THE SUPERCRITICAL STATE OF THE CARBON DIOXIDE AT THE INVESTIGATED REACTION CONDITIONS MAKING THE RAW MATERIAL BETTER ACCESSIBLE AND ACTING AS A SOLVENT ENHANCER. A STATISTICAL APPROACH WAS USED TO FIND THE OPTIMAL REGIONS FOR ALL OPERATING PARAMETERS. TEMPERATURE, PRESSURE AND TIME HAD SIGNIFICANT INFLUENCE ON THE RESULTS. ADDITIONAL TESTS WERE DONE TO EVALUATE THE CONTRIBUTIONS OF VARIOUS ADDITIVES AND AUXILIARIES NAMELY ACIDS AND BASES AND IT WAS FOUND TO BE POSSIBLE EXCHANGING ETHANOL FOR METHANOL WHAT CAN SAVE UP TO TWENTY PERCENT IN THE OVERALL SOLVENT COSTS. IT COULD BE SHOWN THAT WITH THIS PROCESS DESIGN IT IS POSSIBLE TO ACHIEVE DELIGNIFICATION TO A GREAT EXTEND WITH SUFFICIENTLY PURE LIGNIN FRACTIONS. FURTHERMORE IT WAS PROVEN THAT NITROGEN

ENRICHMENT, CONVENTIONALLY PERFORMED SUBSEQUENTLY, CAN BE ACCOMPLISHED DURING THE PULPING PROCESS SIGNIFICANTLY REDUCING ENERGY DEMAND. A NITROGEN ENRICHMENT OF 4% ON AVERAGE WITHIN THE LIGNIN FRACTIONS IS CONSIDERED TO BE SUFFICIENT FOR THE AIMED PURPOSE OF SOIL IMPROVEMENT PROVIDING A HIGH PORTION OF PLANT-AVAILABLE NITROGEN.

NOTE

SO FAR NOT ALL OBTAINED DATA COULD BE EVALUATED TO CHARACTERIZE THE PRODUCT STREAMS IN A MORE COMPREHENSIVE WAY. MANY MORE METHODS E.G. ^{31}P-NMR, ^{15}N-NMR, ATR-IR-SPECTROSCOPY AND SCANNING ELECTRON MICROSCOPY (SEM) HAVE BEEN APPLIED. THESE DATA WILL BE PRESENTED IN THE ASSOCIATED PAPER, WHICH WILL BE SUBMITTED LATER THIS YEAR.

SOME OF THE PRELIMINARY RESULTS OF THIS PROJECT HAVE BEEN PRESENTED AT THE 11TH AIChE SPRING MEETING & 7TH GLOBAL CONGRESS ON PROCESS SAFETY AND AT THE 241ST ACS NATIONAL MEETING & EXPOSITION IN SPRING OF THIS YEAR AND HAVE BEEN PUBLISHED IN THE RESPECTIVE BOOK OF ABSTRACTS (SEE BELOW).

Schrems, M.; Vejdovszky, P.; Zeilinger, M.; Bednarik, S.; Haimer, E.; Liebner, F.; Rosenau, T.; Potthast, A. (2011) Organosolv revisited – biomass valorization with new perspectives. Conference Proceedings, 11th AIChE Spring Meeting & 7th Global Congress on Process Safety, Chicago, IL, United States, March 13-17, 2011.

Liebner, F.; Pour, G.; Klinger, K.; Schrems, M.; Tyhoda, L.; Potthast, A.; Rosenau, T. (2011) Ammonoxidation meets biorefinery: A promising approach for valorizing ligneous materials and combating global desertification. Abstract of Papers, 241st ACS National Meeting & Exposition, Anaheim, CA, United States, March 27-31, 2011.

2.1.2 MODEL SUBSTANCE STUDY

THIS PROJECT AROSE IN CONSEQUENCE OF THE FINDING, THAT SUPERCRITICAL CARBON DIOXIDE ENHANCES THE ACHIEVABLE LIGNIN OUTPUT DURING ORGANOSOLV PULPING. EXPERIMENTS DURING THE PROCESS DEVELOPMENT APPLYING NITROGEN INSTEAD OF CARBON DIOXIDE INDICATED THAT THIS EFFECT IS NOT MERELY A RESULT OF HIGH PRESSURE, ALTHOUGH RESULTS WERE HIGHER COMPARED TO EXPERIMENTS CONDUCTED ONLY UNDER VAPOR PRESSURE OF THE SOLVENTS. IN ORDER TO UNDERSTAND THIS EFFECT IN MORE DETAIL, A MODEL SUBSTANCE STUDY UTILIZING APOCYNOL AS A SIMPLE MONOMERIC MODEL FOR LIGNIN HAS BEEN CARRIED OUT. ALTHOUGH THE SIGNIFICANCE IS LIMITED BY THE FACT, THAT A MONOMER MODEL SUBSTANCE DOES NOT ALLOW INVESTIGATION OF THE ETHER BOND CLEAVAGE AND HENCE DEPOLYMERIZATION, VALUABLE INFORMATION'S COULD BE OBTAINED WHICH ARE SUMMARIZED IN THE FOLLOWING.

SUMMARY

IN THIS STUDY IT COULD BE SHOWN THAT APOCYNOL REACTS VIA A QUINONE METHIDE INTERMEDIATE WHICH IS STABILIZED BY FORMATION OF AN α–ETHYL ETHER THROUGH ADDITION OF ETHANOL AND NOT BY A [1,7]-SIGMATROPIC SHIFT, SEE SCHEME 1.
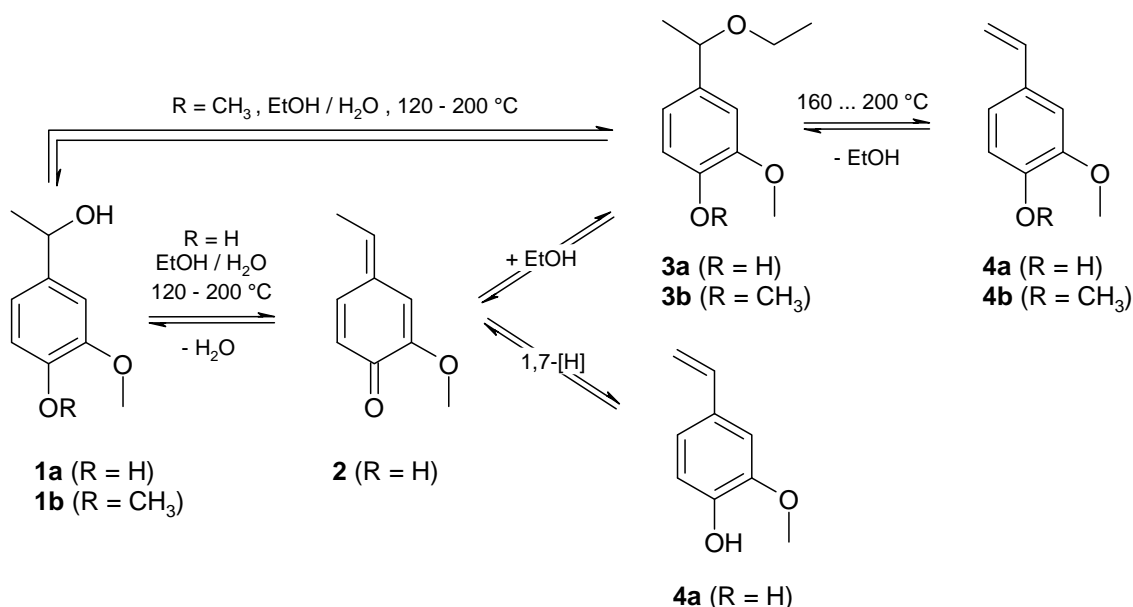
SCHEME 1. EQUILIBRIUM REACTIONS OF THE MONOMERIC MODEL COMPOUNDS **1a** AND **1b** UNDER ORGANOSOLV CONDITIONS (ETHANOL/WATER, 50/50 (V/V), 120-200°C).

THIS α–ETHYL ETHER WAS FOUND TO BE THE MAIN PRODUCT WHEREBY HIGHER REACTION TEMPERATURES AND LONGER REACTION TIMES CAUSE 4-VINYLGUAIACOL TO BECOME THE DOMINATING PRODUCT. REPLACEMENT OF THE PHENOLIC GROUP IN THE MODEL COMPOUND BY A METHOXY GROUP LEADS TO THE ALWAYS OBSERVED SIGNIFICANTLY REDUCED REACTIVITY, WHICH CAN BE EXPLAINED WITH ITS INABILITY TO FORM THE INTERMEDIARY QUINONE METHIDE (**2**).

KINETIC STUDIES ON THE MONOMERIC MODEL COMPOUND APOCYNOL WITH AND WITHOUT SUPERCRITICAL CARBON DIOXIDE AT DIFFERENT TEMPERATURES REVEALED, THAT THE USE OF SUPERCRITICAL CARBON DIOXIDE DURING THE PULPING PROCESS ACCELERATES NOT ONLY THE DECAY OF THE MODEL SUBSTANCE BUT ALSO LOWERS THE ACTIVATION ENERGY FOR THIS REACTION DISTINCTLY, INDICATED IN **FIGURE 16**.
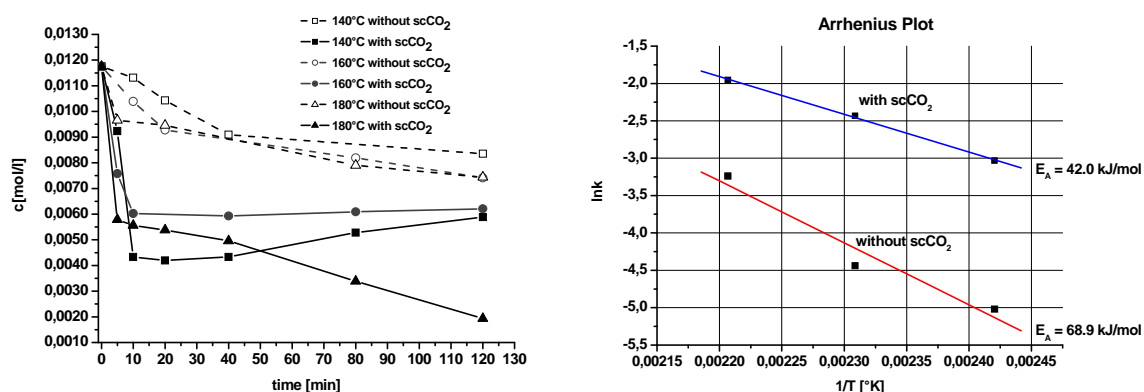
FIGURE 16. *LEFT: KINETICS OF APOCYNOL (**1a**) DEGRADATION AT DIFFERENT TEMPERATURES WITH AND WITHOUT scCO$_2$. RIGHT: RESPECTIVE ARRHENIUS PLOT.*

IN ADDITION TO ITS AIDING EFFECTS IN BIOMASS PENETRATION, THESE RESULTS SUPPORT THE USE OF SUPERCRITICAL CARBON DIOXIDE AS A PULPING ENHANCER IN AN ORGANOSOLV PROCESS AIMING FOR MAXIMUM DELIGNIFICATION BY AFFECTING THIS PROCESS IN A DIRECT MANNER.

MORE RESULTS CAN BE FOUND IN THE MANUSCRIPT, WHICH IS GOING TO BE SUBMITTED IN AUGUST OF THIS YEAR (SEE BELOW).

> *Schrems, M.; Liebner, F.; Betz, M.; Zeilinger, M.; Rosenau, T.; Potthast, A. (2011) Understanding the impact of super critical carbon dioxide on the delignification mechanism during organosolv pulping – a model substance study. Manuscript in preparation for J. Wood. Chem. Technol.*

NOTE

SOME OF THE PRELIMINARY RESULTS OF THIS PROJECT HAVE BEEN PRESENTED AT THE 11TH AICHE SPRING MEETING & 7TH GLOBAL CONGRESS ON PROCESS SAFETY IN SPRING OF THIS YEAR AND HAVE BEEN PUBLISHED IN THE RESPECTIVE BOOK OF ABSTRACTS (SEE BELOW).

> *Schrems, M.; Vejdovszky, P.; Zeilinger, M.; Bednarik, S.; Haimer, E.; Liebner, F.; Rosenau, T.; Potthast, A. (2011) Organosolv revisited – biomass valorization with new perspectives. Conference Proceedings, 11th AIChE Spring Meeting & 7th Global Congress on Process Safety, Chicago, IL, United States, March 13-17, 2011.*

2.2   IONIC LIQUIDS & RENEWABLE RESOURCES

ONE OF THE LARGEST OBSTACLES ON THE WAY TO APPLICABLE TECHNOLOGIES IS THE UNAVAILABILITY OF SOLVENTS CAPABLE TO ENTIRELY DISSOLVE LIGNOCELLULOSIC MATERIALS IN THEIR PRISTINE STATE. EVEN FOR CELLULOSE, ONE OF THE MAIN CONSTITUENTS OF SUCH FEEDSTOCK'S, ONLY A VERY LIMITED NUMBER OF SOLVENT SYSTEMS, SUCH AS *N,N*-DIMETHYLACETAMIDE (DMAC) / LITHIUM CHLORIDE (LICL), *N*-METHYL-2-PYRROLIDINE (NMP) / LITHIUM CHLORIDE, 1,3-DIMETHYL-2-IMIDAZOLIDINONE (DMI) / LITHIUM CHLORIDE, DIMETHYL SULFOXIDE (DMSO)/TETRABUTHYLAMMONIUM FLUORIDE (TBAF) OR *N*-METHYLMORPHOLINE-*N*-OXIDE (NMMO) ARE KNOWN CAPABLE TO DISSOLVE CELLULOSE WITHOUT PRIOR MODIFICATION [KLEMM ET AL. 1998; CAO ET AL. 2009]. HOWEVER, THE FIRST CELLULOSE SOLVENT, SCHWEIZER'S REAGENT, A COPPER-CONTAINING METAL COMPLEX (CUOXAM OR CUPRAMMONIUM HYDROXIDE) AND NAMED AFTER HIS INVENTOR, HAS BEEN DISCOVERED ALREADY MORE THAN 150 YEARS AGO [SCHWEIZER 1857]. HOWEVER, ALL OF THESE SOLVENTS LACK IN DISSOLVING CAPABILITY, TOXICITY AND UNCONTROLLABLE SIDE REACTIONS JUST TO NAME A FEW. TO OVERCOME THESE LIMITATIONS, STRONGLY INTERACTING SOLVENTS ARE NEEDED THAT ARE, IN THE BEST CASE, ALSO CAPABLE TO DISSOLVE THE WHOLE NATURAL SURROUNDING MATRIX.

IONIC LIQUIDS WERE FOUND TO HAVE A HIGH POTENTIAL AS POWERFUL CELLULOSE SOLVENTS WITH THE FIRST REPORT ATTRIBUTED TO CHARLES GRAENACHER WITH HIS U.S. PATENT ABOUT THE DISSOLUTION OF CELLULOSE IN N-ALKYLPYRIDINIUM SALTS IN 1934 [GRAENACHER 1934]. THE RATHER HIGH MELTING POINT OF THESE SALTS (118°C), WHICH IS ABOVE THE CURRENT DEFINITION OF IONIC LIQUIDS (MP < 100°C), AND DOUBTS ABOUT THE VALIDITY OF THESE RESULTS RECENTLY RAISED BY SUN ET AL. RENDERS SWATLOSKI ET AL. AS THE FIRST TO SHOW TRUSTWORTHY THE CAPABILITY OF SOME IONIC LIQUIDS TO DISSOLVE CELLULOSE IN ITS GENUINE FORM [2011; 2002]. ACCORDING TO LITERATURE, THIS POTENTIAL IS PARTICULARLY CONNECTED TO IONIC LIQUIDS CONTAINING AMMONIUM, PYRIDINIUM OR IMIDAZOLIUM CATIONS, HENCE NITROGEN-BASED CATIONS [HONGLU AND TIEJUN 2006; EL SEOUD ET AL. 2007; ZHU ET AL. 2006; LIEBERT, 2010]. PHOSPHONIUM AND SULFONIUM BASED IONIC LIQUID CATIONS DO NOT BEHAVE SIMILARLY WELL IN THIS REGARD. ADDITIONALLY, AN ASYMMETRIC ANION IS REQUIRED TO FORM MELTS WITH CELLULOSE. OUT OF THE NITROGEN-BASED IONIC LIQUID CATIONS CURRENTLY AVAILABLE, IMIDAZOLIUM SEEMS TO BE THE MOST SUITABLE ONE FOR CELLULOSE PROCESSING AS PYRIDINIUM IONIC LIQUIDS BEING DEGRADED IF NO PROTECTIVE GAS IS APPLIED [BARTHEL AND HEINZE 2006]. MOREOVER, SELECTED IONIC LIQUIDS WERE SHOWN TO HAVE THE ABILITY TO DISSOLVE ALSO OTHER MAIN CONSTITUENTS OF LIGNOCELLULOSIC FEEDSTOCK'S SUCH AS LIGNIN E.G. ACCESSIBLE BY SELECTIVE IONIC LIQUID EXTRACTION FROM WOOD [PU ET AL. 2007; LEE ET AL. 2009]. REMARKABLY, THIS DISSOLUTION ABILITY IS NOT ONLY GIVEN FOR ISOLATED COMPONENTS, BUT ALSO FOR THEIR NATURAL MIXTURES OR COMPOSITES. THIS APPLIES EVEN TO NON-MODIFIED WOOD [KILPELAINEN ET AL. 2007].

In this regard, Zavrel et al. found 1-allyl-3-methylimidaolium chloride and 1-ethyl-3-methylimidazolium acetate as the prevailing solvents for this purpose, as a result of their developed high-throughput screening system for ionic liquids dissolving (ligno-)cellulose [2009]. Out of these two, the latter one was found to be superior over the first one as a consequence of a missing reactive side group and more desirable properties as 1-ethyl-3-methylimidazolium acetate is considered non-toxic, non-corrosive and even biodegradable [Liebert 2010]. This finding is consistent with the results published by Brandt et al. who also found this ionic liquid as the most effective one for wood pretreatment and dissolution allegeable by its high hydrogen bond basicity, expressed through the Kamlet-Taft polarity parameter β [2010]. Water content, among other parameters, was found to affect the dissolution process significantly which has been already published by Mazza et al. for cellulose in ionic liquids and was also shown for other cellulose solvents like DMAc/LiCl previously [2009; Röder et al. 2002]. Li et al. found a lower wood density and a larger accessible surface area beneficial for the dissolution performance of ionic liquids and Nakamura et al. argued that even the present atmosphere can affect the liquefaction and depolymerization of wood in ionic liquids [2010; 2010].

In 2007, Kilpelainen et al. found that cellulose can be precipitated after dissolution in ionic liquids by applying suitable anti-solvents like water [Kilpelainen 2007]. In the following, anti-solvent systems e.g. 1:1 ratio of acetone and water [Sun et al. 2009] or acetone and ethanol [Balensiefer et al. 2008; Balensiefer 2008] have been published, allowing separation of dissolved lignocellulosic materials in a cellulose-rich fraction and carbohydrate-free lignin, at least to a certain extend. Sun et al. further reported comparable delignification with the Kraft process when two pretreatment cycles were performed but at lower temperature and pressure and without a high demand of caustic and other chemicals [2009]. Moreover they found also for this system the typical transformation of the naturally occurring cellulose I polymorph into the more stable cellulose II during regeneration. This is in accordance to Zhai et al. who reported identical findings for the ionic liquid 1-butyl-3-methylimidazolium chloride [2007].

Not much is known about the mechanism of cellulose dissolution in ionic liquids rendering its investigation as one of the most important tasks to understand their interaction and potentially design tailored solvents for this purpose. Mäki-Arvela et al. summarized currently available data about the dissolution mechanism comprising only 1-butyl-3-methylimidazolium chloride as the most extensively investigated ionic liquid, and 1-ethyl-3-methylimidazolium acetate

AS THE MOST APPLICABLE ONE FOR BIOMATERIAL PROCESSING [2010]. THEY CITED REMSING ET AL., WHO REPORTED THAT THE CHLORIDE ANION CAN INTERACT IN A 1:1 STOICHIOMETRY WITH THE HYDROXYL GROUPS OF THE CELLULOSIC SUGAR BACKBONE BASED ON ^{13}C AND $^{35/37}$Cl NMR SPECTROSCOPY [2006]. THE LATTER ONE HAS BEEN INVESTIGATED PREVIOUSLY BY ZHANG ET AL. WHO ALSO FOUND VIA NMR SPECTROSCOPY, THAT THE HYDROGEN BONDS BETWEEN THE AROMATIC PROTONS OF THE CATION AND THE HYDROXYL GROUPS OF SUGAR BACKBONE ARE RESPONSIBLE FOR THE OCCURRING SOLVATION PROCESS [2010].

THE MAJOR DRAWBACK OF BIOMASS PROCESSING IN IONIC LIQUIDS BESIDE MANY EXCITING OPPORTUNITIES IS THE CHALLENGING RECYCLING OF THE SOLVENT. ALTHOUGH SOME GROUPS HAVE REPORTED SUCCESSFUL DISTILLATION AND EVEN FRACTIONATED DISTILLATION OF IONIC LIQUID MIXTURES (SEE CHAPTER 1.2.3), THESE PURIFICATION STEPS ARE VERY UNLIKELY TO BE INTEGRATED IN A LARGE SCALE PROCESS DUE TO THEIR HIGH ENERGY DEMAND UNLESS CURRENT IONIC LIQUID ACQUISITION COSTS REMAIN. EXTRACTION WITH COMMON ORGANIC SOLVENTS IS ALSO NOT VERY DESIRABLE AS IT WOULD ELIMINATE EVEN THE SMALLEST "GREEN" ASPECT OF SUCH A PROCESS. SOME RECOMMEND SIMPLE EVAPORATION OF REMAINING SOLVENT RESIDUES PRIOR TO REUSE OF THE IONIC LIQUID [SUN ET AL. 2009], WHEREAS OTHERS CLAIM PURIFICATION UNNECESSARY AT ALL BY REPORTING IONIC LIQUID CIRCULATION WITHOUT ANY DECREASE IN QUALITY [VARANASI ET AL. 2008]. HOWEVER, OWING TO THE HIGH SOLVENT POWER OF IONIC LIQUIDS, ALL KIND OF DEGRADATION PRODUCTS, COMING EITHER FROM THE DISSOLVED MATERIAL OR THE IONIC LIQUID ITSELF [SCHREMS ET AL. 2010], ARE EXPECTED TO ACCUMULATE DURING PROCESSING, MAKING A CONSTANT PURITY AND HENCE QUALITY OF THE RECYCLED IONIC LIQUID VERY UNLIKELY. UNTIL NOW, SUFFICIENT RECYCLING AND PURIFICATION OF THE PROCESSED IONIC LIQUIDS IS STILL NOT AVAILABLE AND REMAINS AS ONE OF THE MOST CHALLENGING OBSTACLES ON THE WAY TO A PROCESS REALIZATION ON A LARGE SCALE [LI ET AL. 2010].

APPLICATIONS OF IONIC LIQUIDS IN BIOMASS PROCESSING ARE MANIFOLD AND ARE THE REASON FOR THE STILL INCREASING INTEREST IN THIS RESEARCH AREA. THE ABILITY OF CERTAIN IONIC LIQUID TO CO-DISSOLVE CELLULOSE WITH FUNCTIONAL ADDITIVES OR COMPOSITE PRODUCTS RENDERS IONIC LIQUIDS AS AN INTERESTING PROCESSING ENVIRONMENT FOR BIOACTIVE SUPPORTS E.G. PREPARATION OF SUPPORTED ENZYME SYSTEMS, MEMBRANE SENSORS OR CELLULOSE/POLYMER BLENDS [SUN ET AL. 2011]. THE CAPABILITY TO DISSOLVE ALSO OTHER BIOMACROMOLECULES SUCH AS CHITIN OR STARCH MAKE THIS SOLVENT CLASS EVEN MORE INTERESTING FOR FUTURE RESEARCH.

PROBABLY THE MOST ASTONISHING FEATURE OF SELECTED IONIC LIQUIDS IS THEIR ABILITY TO DISSOLVE WOOD. THERE IS NO OTHER SOLVENT KNOWN UNTIL TODAY CAPABLE DECRYSTALLIZING AND SOLUBILIZING UNTREATED WOOD EVEN IN THE SHAPE OF RATHER

LARGE CHIPS WHILE PRESERVING THE CHEMICAL INTEGRITY OF ITS CONSTITUENTS DURING DISSOLUTION. ONLY ONE RATHER COMPLEX DISSOLUTION PROCEDURE FOR WOOD NMR, DEVELOPED IN JOHN RALPHS RESEARCH AT THE UNIVERSITY OF WISCONSIN, MADISON IS CAPABLE TO ACHIEVE THIS GOAL [YELLE ET AL. 2006]. IN THIS PROCEDURE, WOOD IS TREATED WITH A MIXTURE OF DMSO AND N-METHYLIMIDAZOLE (NMI) FOLLOWED BY IN SITU ACETYLATION OF THE WOOD CELL WALL, WHICH FULLY SOLUBILIZES THE MATERIAL IN CHLOROFORM. APPLICATIONS OF IONIC LIQUID SOLVENTS RANGE FROM BIOMASS PRETREATMENT FOR ENHANCED ENZYMATIC DEPOLYMERIZATION IN BIOFUEL PRODUCTION OVER EXTRACTION OF CELLULOSE OR LIGNIN OUT OF WOOD WASTES TO EMPLOYMENT AS WOOD PRESERVATIVE AGAINST ATTACK BY INSECTS OR MICRO-ORGANISM [HAN ET AL. 2009]. OTHER APPLICATIONS ARE DISSOLUTION OF LIGNOCELLULOSIC MATERIALS AND SUBSEQUENT FRACTIONATION OF ALL THREE MAJOR BIOMASS COMPONENTS, FUNCTIONALIZATION OF DISSOLVED CELLULOSE OR LIGNOCELLULOSE OR HYDROLYSIS AND TRANSFORMATION INTO PLATFORM CHEMICALS [SUN ET AL. 2011].

SELECTED RESEARCH PROJECTS TOWARDS THE APPLICABILITY OF IONIC LIQUID IN CONTEXT OF CELLULOSE MODIFICATION AND BIOMASS PROCESSING CONDUCTED WITHIN THIS THESIS WILL BE PRESENTED IN THE FOLLOWING CHAPTERS. ALL RESULTS HAVE BEEN ALREADY PUBLISHED OR ARE SUBMITTED FOR PUBLICATION.

2.2.1   SIDE REACTIONS IN IONIC LIQUIDS

THIS PROJECT CAME UP WITH THE INCREASING INTEREST OF IONIC LIQUID AS CELLULOSE SOLVENT AND MEDIA FOR CELLULOSE DERIVATIZATION, MODIFICATION AND CELLULOSE CHEMISTRY IN GENERAL. SIMPLE DERIVATIZATION REACTIONS E.G. ESTERIFICATION, METHYLATION, (TRIMETHYL-) SILYLATION AND ACETYLATION ARE COMMON CELLULOSE MODIFICATIONS WHICH CAN ALSO BE CONDUCTED IN IONIC LIQUIDS. UNLIKE OFTEN ASSUMED, IONIC LIQUIDS ARE NOT INERT SOLVENTS AND REACTION MEDIA IN GENERAL. OWING TO THEIR IMMENSE VARIETY AS A RESULT OF AN ALMOST INFINITE NUMBER OF POSSIBLE CATION-ANION COMBINATIONS, THEY CAN BEHAVE AS BOTH, INERT OR NOT. UNFORTUNATELY BOTH, THE CATION [EBNER ET AL. 2008] AND THE ANION OF 1-ALKYL-3-METHYLIMIDAZOLIUM IONIC LIQUIDS CAN REACT WITH CELLULOSE WHEREFORE CAREFUL SELECTION OF SUITABLE ION-COMBINATIONS IS ESSENTIAL TO ACHIEVE GOOD CONVERSION RATES BY AVOIDING POTENTIAL SIDE REACTIONS BETWEEN THE SOLVENT AND THE SOLUTE. MOST RESULTS OF THIS STUDY HAVE BEEN ALREADY PUBLISHED (SEE BELOW).

SOME ADDITIONAL, UNPUBLISHED RESULTS REGARDING POSSIBLE SIDE REACTION OF THE IONIC LIQUID ANION WILL BE PRESENTED IN THE FOLLOWING:

WITHIN THIS PUBLICATION IT WAS SHOWN, THAT METHYLATION WITH COMMON METHYLATIONS AGENTS SUCH AS METHYL IODIDE OR DIMETHYLSULFATE CONDUCTED IN 1-ALKYL-3-METHYLIMIDAZOLIUM IONIC LIQUIDS WITH CHLORIDE OR ACETATE AS COUNTERION DO NOT LEAD TO THE DESIRED MODIFICATION OF CELLULOSE. SIDE REACTIONS WITH THE SOLVENT IN BOTH CASES GENERATE INACTIVE OR LESS ACTIVE REACTION PRODUCTS MAKING A SATISFYING CONVERSION VERY UNLIKELY. FORTUNATELY, AS INDICATED IN **FIGURE 17**, EFFECTIVE METHYLATION IS POSSIBLE IN THESE IONIC LIQUIDS BY APPLYING DIAZOMETHANE OR ITS DERIVATIVE TRIMETHYLSILYL DIAZOMETHANE (TMS-DAM) AS METHYLATING AGENTS.
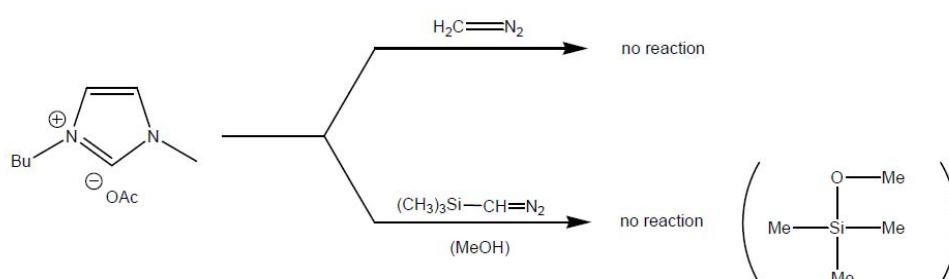

FIGURE 17. NO SIDE REACTION OCCURS BETWEEN 1-ALKYL-3-METHYLIMIDAZOLIUM CHLORIDE OR ACETATE, WHEN DIAZOMETHANE OR TMS-DAM IS APPLIED AS METHYLATING AGENT.

As diazomethane is a rather disliked methylation agent due to its physiological properties and limited storability, it cannot be considered as a suitable replacement for common methylation agents. In contrast to this, TMS-DAM turned out to be a very promising alternative as it is much more convenient to handle and does also not show any side reaction with the solvent. Unlike often reported in literature, also no artifacts e.g. trimethylsilylesters are formed as possible side products when methylation of free acids is attempted [Park et al. 2001]. Moreover, the usually recommended addition of methanol to avoid these artifacts is not necessary in this case [Leggio et al. 2009]. Quite the contrary it leads to formation methoxytrimethylsilane.

Acetylation is another very important if not the most important derivatization step in cellulose chemistry. Numerous experiments have been carried out in imidazolium-based ionic liquids with acetic anhydride as acetylating agent. In most cases this works properly even without base catalysis just by dissolving cellulose in the ionic liquid at elevated temperatures and addition of five equivalents of the acetylating agent [Wu et al. 2004; Schlufter et al. 2006]. Others stated that significant degradation occurs if pyridine isn't added in comparable amounts [Xie et al. 2007]. Köhler et al. previously showed that very efficient acetylation of cellulose can be achieved by reactive intermediates formed with acid chlorides [2007]. This finding led to the question, if simply dissolution of cellulose in the ionic liquid 1-butyl-3-methylimidazolium acetate causes already acetylation without any further addition of reactants as this ionic liquid is usually described as basic. Additionally we found, that degradation products derived from the ionic liquid cation as a result of thermal degradation e.g. imidazole, could act as a base and potentially catalyze such reactions [Schrems et al. 2010].

To verify if this reaction is possible or not, D-glucose was used as a model compound. Surprisingly, no formation of glucose acetate could be observed, neither under uncatalyzed nor under catalyzed conditions adding pyridine as base. Also the supposed formation of N-acetyl imidazole, a potential reaction product of the ionic liquid cation and a strong acetylating agent itself, could not be observed, even after addition of imidazole under various conditions (100°C, 1-24h).

All these mentioned experiments have been carried out in the same way as comparable experiments in the publication and have been analyzed with the same equipment.

2.2.2 Ionic Liquids as Media for Biomass Processing

This project was intended to gain a better understanding of the dissolution behaviour of renewable materials in ionic liquids. The high potential of ionic liquids as powerful cellulose and lignocellulose solvents make it extremely important, to uncover and characterize the so far scarcely investigated dissolution process. Several lignocellulosic materials have been dissolved in 1-ethyl-3-methylimidazolium acetate, which is currently the most common cation-anion combination for this purpose, fractionated by selective precipitation and the obtained products subsequently characterized by analytical means. this study led to a couple of interesting observations whereby especially time-dependent dissolution experiments brought some light into the poorly understood behaviour of lignocellulosic materials in ionic liquids. The results of this study are summarized below.

Summary

In this study it could be confirmed, that certain ionic liquids e.g. 1-ethyl-3-methylimidazolium acetate have the ability to dissolve lignocellulosic materials (wood, straw) and that fractionation of the constituents can be effectuated when the right anti-solvents are applied for precipitation. Two slightly different anti-solvent mixtures (precipitation baths) have been applied and were found to be equally performing regarding achievable fractionation efficiency, see **Figure 18**.
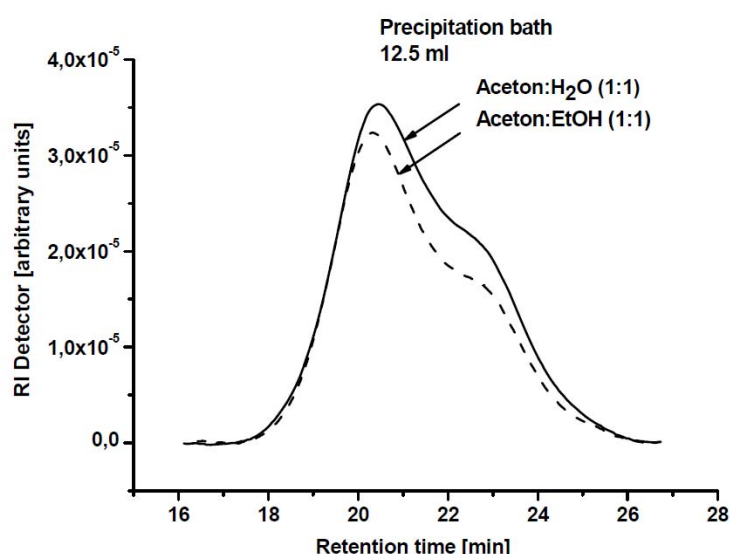

***Figure 18**. GPC elution profiles (0.9% DMAc/LiCl) of the comparison between different cellulose precipitation procedures from ILs.*

The precipitated pure lignins (96-99%) were shown to keep their chemical composition, as the native ratios of H/G/S units remain unaltered.

UNEXPECTEDLY, THE MWDS WERE FOUND TO BE NOT CONSTANT IN THE COURSE OF TIME-DEPENDENT DISSOLUTION EXPERIMENTS. IT COULD BE SHOWN THAT THIS IS NOT A CONSEQUENCE OF PREFERENTIAL DISSOLUTION BUT OF PROGRESSING DEGRADATION OF THE CELLULOSE IN IONIC LIQUID. AS INDICATED IN **FIGURE 19**, THIS EFFECT IS MORE PRONOUNCED IN PURE ILS AND AT HIGHER TEMPERATURES.
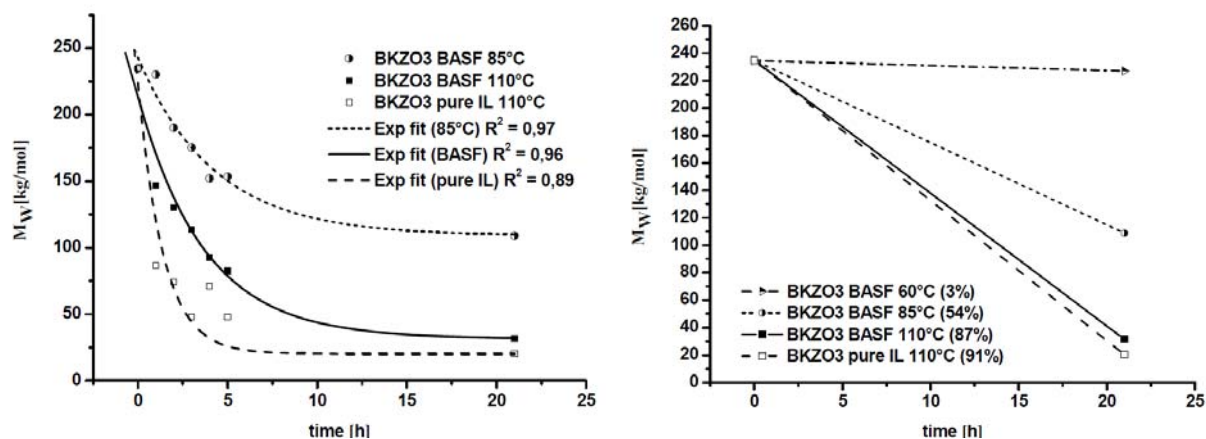
FIGURE 19. M_W BEHAVIOR AFTER COMPLETE DISSOLUTION. LEFT: DEGRADATION OF OZONE BLEACHED BEECH SULFITE PULP (BBSP) IN ILS AFTER COMPLETE DISSOLUTION, INDICATING A STRONG TEMPERATURE DEPENDENCY. RIGHT: TEMPERATURE-DEPENDENT CELLULOSE DEGRADATION IN ILS IN PERCENTAGE OF ORIGINAL M_W.

A COMPREHENSIVE REPORT ABOUT THIS STUDY INCLUDING EXPERIMENTAL DETAILS AND MORE RESULTS CAN BE FOUND IN THE PUBLICATION CITED BELOW.

Schrems, M.; Brandt, A.; Welton, T.; Liebner, F.; Rosenau, T.; Potthast, A. **(2011)** *Ionic liquids as media for biomass processing: opportunities and restrictions.* Holzforschung 65(4), 527-533.

2.2.3 Ionic Liquid Pretreatment of Wood Chips

This study was part of a short term scientific mission from October 15TH 2010 until January 15TH 2011 at Imperial College London. The aim of this project was to answer the question whether ionic liquid pretreatment of wood chips prior to mechanical grinding can reduce the energy demand and thus make the overall biorefinery concept more cost effective. Previous investigations showed considerable swelling and partial dissolution of wood chips in certain ionic liquids, particularly with strong hydrogen-bonding anions. As grinding is considered to constitute the greatest cost of the overall process in any biomass process, potential savings in this process step appear very beneficial. For this purpose, three imidazolium-type ionic liquids have been compared regarding their potential to reduce the energy input during grinding. These ionic liquids have been chosen according their ability to cause wood swelling or dissolution and tested under different treatment conditions. The experimental work of this project has been conducted in the research group of Prof. Tom Welton at the Department of Chemistry. The results of this project are summarized in the following.

Summary

The most important observations in this study have been made already at its beginning. First tests with three totally different ionic liquids concerning the ability to swell or dissolve wood showed that the required energy input during grinding is significantly lowered after ionic liquid pretreatment. Surprising in this regard was the fact that all three ionic liquids gave comparable results rendering a swelling or dissolution effect as explanation for this finding rather unlikely. Further tests at different temperatures and reaction times gave comparable results. Simple wetting could be excluded by using various organic solvents such as DMSO, ethanol or water. As both, chemical effects and wetting could be excluded, only physico-chemical properties of the solvent were left to explain the observed effect. As most ionic liquids are rather viscous liquids, comparative tests have been done with silicone oil and other well known lubricants. Pretreatment with this liquids gave identical results and hence revealed the tribological properties of ionic liquids as triggering effect for this observation. All results of this study can be found in the paper below, which has been submitted for publication.

Schrems, M.; *Brandt, A.; Hallett, J.P.; Murphy, R.J.; Potthast, A.; Ray, M.; Rosenau, T.; Welton, T. (2011) Ionic Liquid Pretreatment of Pine Wood Chips for Reduced Energy Input during Grinding. Manuscript submitted to Green Chem.*

3. CONCLUSION AND OUTLOOK

RENEWABLE RESOURCES ARE THE BASIS OF FUTURE TECHNOLOGIES PROVING ENERGY, FUEL AND A VAST AMOUNT OF PLATFORM CHEMICALS, RENDERING THIS RESEARCH AREA AS ONE OF THE MOST IMPORTANT BUT CHALLENGING TASKS FOR FUTURE GENERATIONS. THE CENTRAL POINT OF THIS THESIS WAS THE UTILIZATION AND TRANSFORMATION OF LIGNOCELLULOSIC MATERIALS SUCH AS WOOD, PULP AND ANNUAL PLANTS, WHICH REPRESENT THE LIONS SHARE AMONG RENEWABLE FEEDSTOCK'S AVAILABLE FOR NEARLY EVERY REGION OF THE WORLD DUE TO THEIR GLOBAL ABUNDANCE.

THE FIRST PROJECT WAS INTENDED TO EVALUATE A NEW ORGANOSOLV-BASED BIOREFINERY CONCEPT TOWARDS ITS POTENTIAL TO MAKE BIOMASS CONVERSION MORE ECONOMICALLY FEASIBLE. RENEWABLE RESOURCES SUCH AS RYE STRAW ARE CHEAP FEEDSTOCK'S BUT REQUIRE A HIGH ENERGY INPUT TO CONVERT THEM INTO FOLLOW-UP PRODUCTS. SIMPLE TRANSFORMATION INTO LOW-VALUE BULK PRODUCTS SUCH AS BIOETHANOL OR BIOGAS, WHICH WAS IN THE FOCUS OF INITIAL BIOREFINERY CONCEPTS, ALWAYS STRUGGLED WITH ECONOMIC EFFICIENCY AND IS NO LONGER CONTEMPORARY. CURRENT CONCEPTS FOCUS ON THE (ADDITIONAL) PRODUCTION OF PLATFORM CHEMICALS AND VALUE-ADDED PRODUCTS TO MAKE SUCH A CONCEPT MORE ECONOMICALLY FEASIBLE. PARTICULARLY N-MODIFIED LIGNIN WAS CONSIDERED AS PLATFORM POTENTIALLY CAPABLE TO SATISFY THIS CLAIM. PROGRESSIVE DESERTIFICATION AND EROSION IN CERTAIN AREAS OF THE WORLD CREATE A DEMAND FOR LONGTIME FERTILIZERS TO RESTORE AND IMPROVE THE SOIL QUALITY WHEREBY N-MODIFIED LIGNINS COULD PLAY A CRUCIAL ROLE. THE DESIGNED PROCESS LEADS TO DELIGNIFICATION RATES OF THE PROCESSED LIGNOCELLULOSIC FEEDSTOCK OF UP TO SEVENTY PERCENT AND GENERATES SUFFICIENTLY NITROGEN-ENRICHED AND PURE LIGNIN FOR THE AIMED PURPOSE OF SOIL IMPROVEMENT. SUPERCRITICAL CARBON DIOXIDE WAS FOUND CAPABLE TO CONSIDERABLY INCREASE THE ACHIEVABLE LIGNIN OUTPUT. THE MECHANISM EXPLAINING THE SUPPORTIVE EFFECT OF SUPERCRITICAL CARBON DIOXIDE IS STILL UNKNOWN. FIRST ATTEMPTS TOWARDS THE CLARIFICATION OF THIS MECHANISM HAVE BEEN CONDUCTED BY STUDYING THE DESCRIBED EFFECT ON APOCYNOL, A MONOMERIC LIGNIN MODEL SUBSTANCE. IN THIS STUDY IT COULD BE SHOWN, THAT THE MONOMERIC LIGNIN MODEL IS SIGNIFICANTLY FASTER DEGRADED IN PRESENCE OF SUPERCRITICAL CARBON DIOXIDE AND THAT THE SUBSEQUENT TRANSFORMATION PROCESS INTO AN INTERMEDIATE FOLLOWED BY FORMATION OF THE END PRODUCT IS STRONGLY AFFECTED IN TERMS OF REQUIRED ACTIVATION ENERGY AND STABILITY OF THE OBSERVED COMPOUNDS. FURTHER STUDIES INVESTIGATING THE EFFECT OF SUPERCRITICAL CARBON DIOXIDE ON THE ETHER BOND OF DIMERIC MODEL COMPOUNDS ARE NEEDED, TO UNDERSTAND THE OBSERVED EFFECT AND ITS IMPACT ON LIGNIN DEPOLYMERIZATION ON A MORE COMPREHENSIVE LEVEL.

IONIC LIQUIDS ARE KNOWN TO HAVE A HIGH POTENTIAL IN DISSOLVING CELLULOSE, LIGNOCELLULOSE AND EVEN UNMODIFIED WOOD. THIS UNPARALLELED ABILITY COMBINED WITH UNIQUE, ADJUSTABLE SOLVENT PROPERTIES MADE THEM AN EXTENSIVELY STUDIED SOLVENT AND PROCESSING MEDIA FOR LIGNOCELLULOSIC MATERIALS.

THE FIRST PROJECT IN THIS CONTEXT WAS FOCUSED ON POTENTIAL SIDE REACTIONS OF IONIC LIQUIDS WHICH ARE, AS A CONSEQUENCE OF THEIR APPARENT ENDLESS VARIETY, NOT INERT SOLVENTS ON A GENERAL BASE. CATION-ANION COMBINATIONS NEED TO BE SELECTED CAREFULLY FOR THE RESPECTIVE PURPOSE IN ORDER TO GUARANTEE EFFECTIVE PROCESSING AND AVOID ADVERSE EFFECTS. THIS STUDY SHOWED THAT BOTH CHLORIDE AND ACETATE, WHICH ARE CURRENTLY THE MOST PROMINENT ANIONS FOR 1-ALKYL-3-METHYLIMIDAZOLIUM TYPE IONIC LIQUIDS, CAN LEAD TO NUMEROUS SIDE REACTIONS WHEN COMMONLY PERFORMED DERIVATIZATION REACTIONS OF CELLULOSE AND CELLULOSIC MODEL COMPOUNDS SUCH AS ESTERIFICATION, METHYLATION OR SILYLATION ARE ATTEMPTED IN THIS MEDIA. IN COULD ALSO BE SHOWN E.G. IN CASE OF METHYLATION, THAT SOME OF THESE SIDE REACTIONS CAN BE PREVENTED BY SELECTING SUITABLE REAGENTS IMPLYING AWARENESS OF THESE POTENTIAL PITFALLS.

THE NEXT PROJECT, SETTLED ON THE INTERFACE BETWEEN RENEWABLE RESOURCES AND IONIC LIQUIDS, AIMED FOR A BETTER UNDERSTANDING OF THE DISSOLUTION BEHAVIOUR OF LIGNOCELLULOSIC MATERIALS IN IONIC LIQUIDS INCLUDING SOLUTE STABILITY AND FURTHER PROCESSING. IT COULD BE PROVEN THAT LIGNOCELLULOSIC MATERIALS DISSOLVED IONIC LIQUIDS CAN BE FRACTIONATED IN THEIR MAIN CONSTITUENTS WHEN SUITABLE ANTI-SOLVENTS ARE APPLIED, LEADING TO SPARSELY BUT VERY PURE LIGNIN FRACTIONS. CELLULOSE WAS FOUND TO BE DEGRADED IN IONIC LIQUIDS DURING AND AFTER DISSOLUTION WITH ITS SEVERITY DEPENDENT ON APPLIED TEMPERATURE AND SOLVENT PURITY. MODERATE TEMPERATURES DID NOT CAUSE RECOGNIZABLE DEPOLYMERIZATION WHEREBY ELEVATED TEMPERATURES, MOST OFTEN USED IN LITERATURE, LED TO SEVERE DEGRADATION AND HENCE A REDUCTION IN QUALITY OF THE PROCESSED MATERIAL. MOREOVER, HIGHLY PURIFIED SOLVENTS CAUSED STRONGER DEGRADATION EFFECTS DUE TO THEIR HIGHER REACTIVITY MAKING HIGHLY PURIFIED IONIC LIQUIDS FOR SUCH APPLICATIONS UNNECESSARY OR EVEN DETRIMENTAL.

THE MOST RECENT PROJECT ABOUT IONIC LIQUIDS AS POTENTIAL ENERGY SAVERS IN MECHANICAL SIZE REDUCTION PROCESSES FOR WOOD E.G. GRINDING, UNVEILED THEIR ADDITION PRIOR TO PROCESSING VERY BENEFICIAL. DEPENDENT ON APPLIED TEMPERATURE, RELATIVE ENERGY REDUCTIONS OF UP TO 85% COULD BE ACHIEVED RATHER INDEPENDENT OF THE USED ION-ION-COMBINATION. THIS FACT COULD LATER BE EXPLAINED WITH THE TRIBOLOGICAL PROPERTIES OF IONIC LIQUIDS, WHICH WERE FOUND RESPONSIBLE FOR THIS OBSERVATION. ON THE CONTRARY IT COULD BE SHOWN, THAT UNIQUE FEATURES OF CERTAIN IONIC LIQUIDS TO DECRYSTALLIZE AND SOLUBILIZE

LIGNOCELLULOSIC MATERIALS DO NOT PLAY ANY NOTEWORTHY ROLE IN REDUCING REQUIRED ENERGY DEMAND.

4. LITERATURE

APPETECCHI, G.B.; MONTANINO, M.; CAREWSKA, M.; MORENO, M.; ALESSANDRINI, F.; PASSERINI, S. (**2011**) CHEMICAL-PHYSICAL PROPERTIES OF BIS(PERFLUOROALKYLSULFONYL)IMIDE-BASED IONIC LIQUIDS. *ELECTROCHIM. ACTA* 56, 1300-1307.

ARMSTRONG, J.P.; HURST, C.; JONES, R.G.; LICENCE, P.; LOVELOCK, K.R.J.; SATTERLEY, C.J.; VILLAR-GARCIA, I.J. (**2007**) VAPOURIZATION OF IONIC LIQUIDS. *PHYS. CHEM. CHEM. PHYS.* 9, 982-990.

ATALLA, R.H.; VANDERHART, D.L. (**1984**) NATIVE CELLULOSE: A COMPOSITE OF TWO DISTINCT CRYSTALINE FORMS. *CHEM. SCI. DIV., INST. PAPER CHEM.* 223(4633), 283-285.

ATWOOD, J.L.; ATWOOD, J.D. (**1976**) INORGANIC COMPOUNDS WITH UNUSUAL PROPERTIES. IN: KING, R.B. (ED.) ADVANCES IN CHEMISTRY SERIES NO. 150. AMERICAN CHEMICAL SOCIETY, WASHINGTON, DC, 112-127.

BAKER, S.N.; BAKER, G.A.; KANE, M.A.; BRIGHT, F.V. (**2001**) THE CYBOTACTIC REGION SURROUNDING FLUORESCENT PROBES DISSOLVED IN 1-BUTYL-3-METHYLIMIDAZOLIUM HEXAFLUOROPHOSPHATE: EFFECTS OF TEMPERATURE AND ADDED CARBON DIOXIDE. *J. PHYS. CHEM. B*, 105(39), 9663-9668.

BALENSIEFER, T.; BRODERSEN, J.; D'ANDOLA, G.; MASSONNE, K.; FREYER, S.; STEGMANN, V. (**2008**) METHOD FOR PRODUCING GLUCOSE BY ENZYMATIC HYDROLYSIS OF CELLULOSE THAT CAN BE PRETREATED WITH AN IONIC LIQUID CONTAINING A POLYATOMIC ANION. PCT INT. APPL., WO 2008/090155 A1.

BALENSIEFER, T. (**2008**) METHOD FOR PRODUCING GLUCOSE BY ENZYMATIC HYDROLYSIS OF CELLULOSE THAT IS OBTAINED FROM MATERIAL CONTAINING LIGNO-CELLULOSE USING AN IONIC LIQUID THAT COMPRISES A POLYATOMIC ANION. PCT INT. APPL., WO 2008/090156 A1.

BARTHEL, S.; HEINZE, T. (**2006**) ACYLATION AND CARBANILATION OF CELLULOSE IN IONIC LIQUIDS. *GREEN CHEM.* 8, 301-306.

BONHOTE, P.; DIAS, A.-P.; PAPAGEOTGIOU, N.; KALYANASUNDARAM, K.; GRÄTZEL, M. (**1996**) HYDROPHOBIC, HIGHLY CONDUCTIVE AMBIENT-TEMPERATURE MOLTEN SALTS. *INORG. CHEM.* 35, 1168-1178.

BOON, J.; LEVINSKY, J.A.; PFLUG, J.L.; WILKES, J.S. (**1986**) FRIEDEL-CRAFTS REACTIONS IN AMBIENT-TEMPERATURE MOLTEN SALTS. *J. ORG. CHEM.* 51, 480-483.

BRANDT, A.; HALLETT, J.P.; LEAK, D.J.; MURPHY, R.J.; WELTON, T. (**2010**) THE EFFECT OF THE IONIC LIQUID ANION IN THE PRETREATMENT OF PINE WOOD CHIPS. *GREEN CHEM.* 12, 672-679.

CAO, Y.; WU, J.; LI, H.; ZHANG, Y.; HE, J. (**2009**) ROOM TEMPERATURE IONIC LIQUIDS (RTILS): A NEW AND VERSATILE PLATFORM FOR CELLULOSE PROCESSING AND DERIVATIZATION. *CHEM. ENG. J.* 147(1), 13-21.

CHERUBINI, F. (**2010**) THE BIOREFINERY CONCEPT: USING BIOMASS INSTEAD OF OIL FOR PRODUCING ENERGY AND CHEMICALS. *ENERG. CONVERS. MANAGE.* 51, 1412-1421.

CLARK, J.H.; BUDARIN, V.; DESWARTE, F.E.I.; WILSON, A.J. (**2006**) GREEN CHEMISTRY AND THE BIOREFINERY: A PARTNERSHIP FOR A SUSTAINABLE FUTURE. *GREEN CHEM.* 8, 853-860.

CROWHURST, L.; MAWDSLEY, P.R.; PEREZ-ARLANDIS, J.M.; SALTER, P.A.; T. WELTON, T. (**2003**) SOLVENT-SOLUTE INTERACTIONS IN IONIC LIQUIDS. *PHYS. CHEM. CHEM. PHYS.* 5, 2790-2794.

DALMOLIN, E.; SKOVROINSKI, E.; BIASI, A.; CORAZZA, M.L.; DARIVA, C.; OLIVIEIRA, O. (**2006**) SOLUBILITY OF CARBON DIOXIDE IN BINARY AND TERNARY MIXTURES WITH ETHANOL AND WATER. *FLUID PHASE EQUILIBR.* 245, 193-200.

DEETLEFS, M.; HARDACRE, C.; NIEUWENHUYZEN, M.; PADUA, A.A.H.; SHEPPARD, O.; SOPER, A.K. (**2006**). LIQUID STRUCTURE OF THE IONIC LIQUID 1,3-DIMETHYLIMIDAZOLIUM BIS{(TRIFUOROMETHYL)SULFONYL}AMIDE. *J. PHYS. CHEM. B* 110, 12055-12061.

DEMIRBAS, A. (**2010a**) METHANE HYDRATES AS POTENTIAL ENERGY RESOURCE: PART 1 – IMPORTANCE, RESOURCE AND RECOVERY FACILITIES. *ENERG. CONVERS. MANAGE.* 51, 1547-1561.

DEMIRBAS, A. (**2010b**) METHANE HYDRATES AS POTENTIAL ENERGY RESOURCE: PART 2 – METHANE PRODUCTION PROCESSES FROM GAS HYDRATES. *ENERG. CONVERS. MANAGE.* 51, 1562-1571.

DOHERTY, T.V.; MORA-PALE, M.; FOLEY, S.E.; LINHARDT, R.J.; DORDICK, J.S. (**2010**) IONIC LIQUID SOLVENT PROPERTIES AS PREDICTORS OF LIGNOCELLULOSE PRETREATMENT EFFICACY. *GREEN CHEM.* 12, 1967-1975.

EARLE, M.J.; ESPERANCA, J.M.S.S.; GILEA, M.A.; CANONGIA LOPES, J.N.; REBELO, L.P.N.; MAGEE, J.W.; SEDDON, K.R.; WIDEGREN, J.A. (**2006**) THE DISTILLATION AND VOLATILITY OF IONIC LIQUIDS. *NATURE*, 439, 831-834.

EBNER, G.; SCHIEHSER, S.; POTTHAST, A.; ROSENAU, T. (**2008**) SIDE REACTION OF CELLULOSE WITH COMMON 1-ALKYL-3-METHYLIMIDAZOLIUM-BASED IONIC LIQUIDS. *TET. LETT.* 49, 7322-7324.

EBRINGEROVA, A. (**2006**) STRUCTURAL DIVERSITY AND APPLICATION POTENTIAL OF HEMICELLULOSES. *MACROMOL. SYMP.* 232, 1-12. IN: FISCHER, K.; HEINZE, T. (EDS.) HEMICELLULOSES. WILEY-VCH, WEINHEIM

EL SEOUD, O.A.; KOSCHELLA, A.; FIDALE, L.C.; DORN, S.; HEINZE, T. (**2007**) APPLICATIONS OF IONIC LIQUIDS IN CARBOHYDRATE CHEMISTRY: A WINDOW OF OPPORTUNITIES. *BIOMACROMOL.* 8(9), 2629-2647.

FAIX, O. (**2007**) CHEMIE DES HOLZES. IN: WAGENFÜHR, A.; SCHOLZ, F. (EDS.) TASCHENBUCH DER HOLZTECHNIK. CARL HANSER PUBLISHING, MUNICH

FENGEL, D.; WEGENER, G. (**1989**) WOOD: CHEMISTRY, ULTRASTRUCTURE, REACTIONS. DE GRUYTER, BERLIN

FINK, H.-P.; HOFMANN, D.; PURZ, H.J. (**1990**) ON THE FIBRILLAR STRUCTURE OF NATIVE CELLULOSE. *ACTA. POLYM.* 41, 131-137.

FISCHER, S.; LEIPNER, H.; BRENDLER, E.; VOIGT, W.; FISCHER, K. (**1999**) MOLTEN INORGANIC SALT HYDRATES AS CELLULOSE SOLVENTS. *ACS SYMP. SER.* 737, 143-150.

FISCHER, S.; LEIPNER, H.; THÜMMLER, K.; BRENDLER, E.; PETERS, J. (**2003**) INORGANIC MOLTEN SALTS AS SOLVENTS FOR CELLULOSE. *CELLULOSE* 10, 227-236.

FONSECA, G.S.; UMPIERRE, A.P.; FICHTNER, P.F.P.; TEIXEIRA, S.R.; DUPONT, J. (**2003**) THE USE OF IMIDAZOLIUM IONIC LIQUIDS FOR THE FORMATION AND STABILIZATION OF Ir0 AND Rh0 NANOPARTICLES: EFFICIENT CATALYSTS FOR THE HYDROGENATION OF ARENES. *CHEM. EUR. J.* 9, 3263-3269.

FREIRE, M.G.; CARVALHO, P.J.; FERNANDES, A.M.; MARRUCHO, I.M.; QUEIMADA, A.J.; COUTINHO, J.A.P. (**2007**) SURFACE TENSIONS OF IMIDAZOLIUM BASED IONIC LIQUIDS: ANION, CATION, TEMPERATURE AND WATER EFFECT. *J. COLLOID. INTERF.* SCI. 314, 621-630.

FUKUMOTO, K.; YOSHIZAWA, M.; OHNO, H. (**2005**) ROOM TEMPERATURE IONIC LIQUIDS FROM 20 NATURAL AMINO ACIDS. *J. AM. CHEM. SOC.* 127(8), 2398-2399.

GAO, M.; XU, F.; LI, S.; JI, X.; CHEN, S.; ZHANG, D. (**2010**) EFFECT OF sc-CO_2 PRETREATMENT IN INCREASING RICE STRAW BIOMASS CONVERSION. *BIOSYSTEMS ENG.* 106, 470-475.

GRAENACHER, C. (**1934**) CELLULOSE SOLUTION. U.S. PATENT 1,943,176.

HAN, S.; LI, J.; ZHU, S.; CHEN, R.; WU, Y.; ZHANG, X.; YU, Z. (**2009**) POTENTIAL APPLICATIONS OF IONIC LIQUIDS IN WOOD RELATED INDUSTRIES. *BIORES.* 4(2), 825-834.

HOLBREY, J.D.; ROGERS, R.D. (**2003**) MELTING POINTS AND PHASE DIAGRAMS. IN: WASSERSCHEID, P.; WELTON, T. (EDS.) IONIC LIQUIDS IN SYNTHESIS. WILEY-VCH, WEINHEIM

HONGLU, X.; TIEJUN, S. (**2006**) WOOD LIQUEFACTION BY IONIC LIQUIDS. *HOLZFORSCHUNG* 60(5), 509-512.

HUNT, P.A.; KIRCHNER, B.; WELTON, T. (**2006**) CHARACTERIZING THE ELECTRONIC STRUCTURE OF IONIC LIQUIDS: AN EXAMINATION OF THE 1-BUTYL-3-METHYLIMIDAZOLIUM CHLORIDE ION PAIR. *CHEM. EUR. J.* 12, 6762-6775.

HURLEY, F.H. (**1948**) U.S. PATENT 4,446,331.

IEA (**2008**). IEA BIOENERGY TASK 42 ON BIOREFINERIES: CO-PRODUCTION OF FUELS, CHEMICALS, POWER AND MATERIALS FROM BIOMASS. IN: MINUTES OF THE THIRD TASK MEETING, COPENHAGEN, DENMARK, 25-26 MARCH 2007 HTTP://WWW.BIOREFINERY.NL/IEABIOENERGY-TASK42/

JACOBS, A.; LUNDQVIST, J.; STALBRAND, H.; TJERNELD, F.; DAHLMAN, D. (**2002**) CHARACTERIZATION OF WATER-SOLUBLE HEMICELLULOSES FROM SPRUCE AND ASPEN EMPLOYING SEC/MALDI MASS SPECTROMETRY. *CARBOHYD. RES.* 337, 711-717.

JARVIS, M.C. (**2009**) PLANT CELL WALLS: SUPRAMOLECULAR ASSEMBLY, SIGNALLING AND STRESS. *STRUCT. CHEM.* 20, 245-253.

KAMLET, M.J.; TAFT, R.W. (**1976**) THE SOLVATOCHROMIC COMPARISON METHOD. I. THE β-SCALE OF SOLVENT HYDROGEN-BOND ACCEPTOR (HBA) BASICITIES. *J. AM. CHEM. SOC.*, 98, 377-383.

KILPELAINEN, I.; XIE, H.; KING, A.; GRANSTROM, M.; HEIKKINEN, S.; ARGYROPOULOS, D. (**2007**) DISSOLUTION OF WOOD IN IONIC LIQUIDS. *J. AGRIC. FOOD. CHEM.* 55, 9142-9148.

KLEINERT, T.; TAYENTHAL, K. (**1931**) ÜBER NEUERE VERSUCHE ZUR TRENNUNG VON CELLULOSE UND INKRUSTEN VERSCHIEDENER HÖLZER. *ANGEW. CHEM.* 44, 788-791.

KLEMM, D.; PHILIPP, B.; HEINZE, T.; HEINZE, U.; WAGENKNECHT, W. (**1998**) COMPREHENSIVE CELLULOSE CHEMISTRY; WILEY-VCH, WEINHEIM; VOL. 1&2.

KLEMM, D.; SCHMAUDER, H.-P.; HEINZE, T. (**2002**) CELLULOSE. IN: DE BAETS, S.; VANDAMME, E.J.; STEINBÜCHEL, A. (EDS.) BIOPOLYMERS. WILEY-VCH, WEINHEIM

KLEMM, D.; HEUBLEIN, B.; FINK, H.-P.; BOHN, A. (**2005**) CELLULOSE: FASCINATING BIOPOLYMER AND SUSTAINABLE RAW MATERIAL. *ANGEW. CHEM. INT. ED.* 44, 3358-3393.

KÖHLER, S.; LIEBERT, T.; SCHÖBITZ, M.; SCHALLER, J.; MEISTER, F.; GÜNTHER, W.; HEINZE, T. (**2007**) INTERACTIONS OF IONIC LIQUIDS WITH POLYSACCHARIDES 1. UNEXPECTED ACETYLATION OF CELLULOSE WITH 1-ETHYL-3-METHYLIMIDAZOLIUM ACETATE. *MACROL. RAPID COMMUN.* 28, 2311-2317.

LEE, S.H.; DOHERTY, T.V.; LINHARDT, J.S. (**2009**) IONIC LIQUID-MEDIATED SELECTIVE EXTRACTION OF LIGNIN FROM WOOD LEADING TO ENHANCED ENZYMATIC CELLULOSE HYDROLYSIS. *BIOTECHNOL. BIOENG.* 102(5), 1368-1376.

LEE, S.-Y.; HOLDER, G.D. (**2001**) METHANE HYDRATES POTENTIAL AS A FUTURE ENERGY SOURCE. *FUEL PROCESS. TECHNOL.*, 71, 181-186.

LEGGIO, A.; LIGUORI, A.; PERRI, F.; SICILIANO, C.; VISCOMI, M.C. (**2009**) METHYLATION OF α-AMINO ACIDS AND DERIVATIVES USING TRIMETHYLSILYLDIAZOMETHANE. *CHEM. BIOL. DRUG DES.* 73, 287-291.

LI, B.; ASIKKALA, J.; FILPPONEN, I.; ARGYROPOULOS, D.S. (**2010**) FACTORS AFFECTING WOOD DISSOLUTION AND REGENERATION OF IONIC LIQUIDS. *IND. ENG. CHEM. RES.* 49, 2477-2484.

LIEBERT, T. (**2010**) CELLULOSE SOLVENTS – REMARKABLE HISTORY, BRIGHT FUTURE. IN: CELLULOSE SOLVENTS: FOR ANALYSIS, SHAPING AND CHEMICAL MODIFICATION; LIEBERT ET AL. ACS SYMPOSIUM SERIES, AMERICAN CHEMICAL SOCIETY, WASHINGTON, D.C.

LIEBNER, F.; FISCHER, K.; KATZUR, J.; BÖCKER, L. (**2006**) NOVIHUM[TM] – HIGH-GRADE ARTIFICIAL HUMUS AND LONG-LASTING FERTILIZER FOR ACCELERATED REHABILITATION OF

degraded areas. In: UNESCO office Beijing: The Loess Plateau in Central China: Ecological Restoration and Management. ERSEC Ecological Book Series III, 183-207; Tsinghua University Press, Springer, Beijing; ISBN: 7-302-14094-4.

MacFarlane, D.R.; Golding, J.; Forsyth, S.; Forsyth, M.; Deacon, G.B. (**2001**) Low viscosity ionic liquids based on organic salts of the dicyanamide anion. *Chem. Commun.* (16), 1430-1431.

Mäki-Arvela, P.; Anugwom, I.; Virtanen, P.; Sjöholm, R.; Mikkola, J.P. (**2010**) Dissolution of lignocellulosic materials and its constituents using ionic liquids – A review. *Ind. Crop. Prod.* 32(3), 175-201.

Mantz, R.A.; Trulove, P.C. (**2003**) Viscosity and Density of Ionic Liquids. In: Wasserscheid, P.; Welton, T. (Eds.) Ionic Liquids in Synthesis. Wiley-VCH, Weinheim

Mazza, M.; Catana, D.-A.; Vaca-Garcia, C.; Cecutti, C. (**2009**) Influence of water on the dissolution of cellulose in selected ionic liquids. *Cellulose* 16, 207-215.

Mühlenthaler, K. (**1965**) The fine structure of the cellulose microfibril. In: Cote, W.A. (Ed.) Cellular Ultrastructure of Woody Plants. Syracuse University Press, Syracuse, New York

Muurinen, E. (**2000**) Organosolv pulping. A review and distillation study related to peroxacid. Dissertation, University of Oulu, Oulu, Finland. http://herkules.oulu.fi/isbn9514256611/index.html?lang=en (09.05.2011), ISSN 1796-2226 (Online).

Nakamura, A.; Miyafuji, H.; Saka, S. (**2010**) Influence of reaction atmosphere on the liquefaction and depolymerization of wood in an ionic liquid, 1-ethyl-3-methylimidazolium chloride. *J. Wood Sci.* 56, 256-261.

Öhgren, K.; Bura, R.; Saddler, J.; Zacchini, G. (**2007**) Effect of hemicellulose and lignin removal on enzymatic hydrolysis of steam pretreated corn stover. *Bioresource Technol.* 98, 2503-2510.

Oliet, M.; Garcia, J.; Rodriguez, F.; Gilarranz, M.A. (**2002**) Solvent effects in autocatalyzed alcohol-water pulping – Comparative study between ethanol and methanol as delignifying agents. *Chem. Eng. J.* 87, 157-162.

PAN, X.; GILKES, N.; KADLA, J.; PYE, K.; SAKA, S.; GREGG, D.; EHARA, K.; XIE, D.; LAM, D.; SADDLER, J. (**2006**) BIOCONVERSION OF HYBRID POPLAR TO ETHANOL AND CO-PRODUCTS USING AN ORGANOSOLV FRACTIONATION PROCESS: OPTIMIZATION OF PROCESS YIELDS. *BIOTECHNOL. BIOENG.* 94(5), 851-861.

PARK, Y.; ALBRIGHT, K.J.; CAI, Z.Y.; PARIZA, M.W. (**2001**) COMPARISON OF METHYLATION PROCEDURES FOR CONJUGATED LINOLEIC ACID AND ARTIFACT FORMATION BY COMMERCIAL (TRIMETHYLSISLYL)DIAZOMETHANE. *J. AGRIC. FOOD CHEM.* 49, 1158-1164.

PASQUINI, D.; PIMETA, M.T.B.; FERREIRA, L.H. (**2005**) SUGAR CANE BAGASSE PULPING USING SUPERCRITICAL CO_2 ASSOCIATED WITH CO-SOLVENT 1-BUTANOL/WATER. *J. SUPERCRIT. FLUID.* 34, 125-131.

PRINGLE, J.M.; GOLDING, J.; BARANYAI, K.; FORSYTH, C.M.; DEACON, B.B.; SCOTT, J.L.; MCFARLANE, D.R. (**2003**) THE EFFECT OF ANION FLUORINATION IN IONIC LIQUIDS – PHYSICAL PROPERTIES OF A RANGE OF BIS(METHANESULFONYL)AMIDE SALTS. *NEW J. CHEM.* 27, 1504-1510.

PU, Y.; JIANG, N.; RAGAUSKAS, A.J. (**2007**) IONIC LIQUID AS A GREEN SOLVENT FOR LIGNIN. *J. WOOD CHEM. TECHNOL.* 27(1), 23-33.

REICHARDT, C. (**1992**) SOLVATOCHROMISM, THERMOCHROMISM, PIEZOCHROMISM, HALOCHROMISM, AND CHIRO-SOLVATOCHROMISM OF PYRIDINIUM N-PHENOXIDE BETAINE DYES. *CHEM. SOC. REV.* 21(3), 147-153.

REMSING, R.C.; SWATLOSKI, R.P.; ROGERS, R.D.; MOYNA, G. (**2006**) MECHANISM OF CELLULOSE DISSOLUTION IN THE IONIC LIQUID 1-*n*-BUTYL-3-METHYLIMIDAZOLIUM CHLORIDE: A ^{13}C AND $^{35/37}$Cl NMR RELAXATION STUDY ON MODEL SYSTEMS. *CHEM. COMMUN.* 12, 1271-1273.

RESTOLHO, J.; SERRO, A.P.; MATA, J.L.; SARAMAGO, B. (**2009**) VISCOSITY AND SURFACE TENSION OF 1-ETHANOL-3-METHYLIMIDAZOLIUM TETRAFLUOROBORATE AND 1-METHYL-3-OCTYLIMIDAZOLIUM TETRAFLUOROBORATE OVER A WIDE TEMPERATURE RANGE. *J. CHEM. ENG. DATA*, 54, 950-954.

RÖDER, T.; POTTHAST, A.; ROSENAU, T.; KOSMA, P.; BALDINGER, T.; MORGENSTERN, B.; GLATTER, O. (**2002**) THE EFFECT OF WATER ON CELLULOSE SOLUTIONS IN DMAc/LiCl. *MACROMOL. SYMP.* 190, 151-159.

Röhrling, J.; Potthast, A.; Rosenau, T.; Lange, T.; Ebner, G.; Sixta, H.; Kosma, P. (**2002**) A novel method for determination of carbonyl groups in cellulosics by fluorescence labeling. 1. Method development. *Biomacromol*. 3, 959-968.

Salmen, L.; Olsson, A.-M. (**1998**) Interaction between hemicelluloses, lignin and cellulose: structure-property relationships. *J. Pulp Pap. Sci*. 24(3), 99-103.

Sassner, P.; Galbe, M.; Zacchi, G. (**2005**) Steam Pretreatment of *Salix* with and without SO_2 Impregnation for Production of Bioethanol. *Appl. Biochem. Biotech*. 121-124, 1101-1118.

Schlufter, K.; Schmauder, H.-P.; Dorn, S.; Heinze, T. (**2006**) Efficient Homogenous Chemical Modification of Bacterial Cellulose in the Ionic Liquid 1-*N*-Butyl-3-methylimidazolium Chloride. *Macromol. Rapid Commun*. 27, 1670-1676.

Schrems, M.; Ebner, G.; Liebner, F.; Becker, E.; Potthast, A.; Rosenau, T. (**2010**) Side Reactions in the system Cellulose/1-Alkyl-3-methylimidazolium Ionic Liquid. In: Liebert, T. Heinze, T.; Edgars, K. (Eds.) Cellulose Solvents: For Analysis, Shaping and Chemical Modifications. ACS Symposium Series, American Chemical Society, Washington, D.C.

Schrems, M.; Brandt, A.; Welton, T.; Liebner, F.; Rosenau, T.; Potthast, A. (**2011**) Ionic liquids as media for biomass processing: opportunities and restrictions. *Holzforschung* 65(4), 527-533.

Schubert, W.J. (**1965**) Lignin Biochemistry. Academic Press, New York

Schweizer, E. (**1857**) Das Kupferoxyd-Ammoniak, ein Auflösemittel für die Pflanzenfaser. *J. Prakt. Chem*. 72(1), 109-111.

Seddon, K.R.; Stark, A.; Torres, M.-J. (**2000**) Influence of chloride, water, and organic solvents on the physical properties of ionic liquids. *Pure Appl. Chem*. 72(12), 2275-2287.

Shafiee, S.; Topal, E. (**2009**) When will fossil fuel reserves be diminished? *Energ. policy*, 37, 181-189.

Sugiyama, J.; Vuong, R.; Chanzy, H. (**1991**) Electron diffraction study on the crystalline phases occurring in native cellulose from an algal cell wall. *Macromolecules*, 24, 4168-4175.

SUN, N.; RAHMAN, M.; QIN, Y.; MAXIM, M.L.; RODRIGUEZ, H.; ROGERS, R.D. (**2009**) COMPLETE DISSOLUTION AND PARTIAL DELIGNIFICATION OF WOOD IN THE IONIC LIQUID 1-ETHYL-3-METHYLIMIDAZOLIUM ACETATE. *GREEN CHEM.* 11, 646-655.

SUN, N.; RODRIGUEZ, H.; RAHMAN, M.; ROGERS, R.D. (**2011**) WHERE ARE IONIC LIQUID STRATEGIES MOST SUITED IN THE PURSUIT OF CHEMICALS AND ENERGY FROM LIGNOCELLULOSIC BIOMASS? *CHEM. COMMUN.* 47, 1405-1421.

SWATLOSKI, R.P.; SPEAR, S.K.; HOLBREY, J.D.; ROGERS, R.D. (**2002**) DISSOLUTION OF CELLULOSE WITH IONIC LIQUIDS. *J. AM. CHEM. SOC.* 124, 4974-4975.

TABUCHI, M.; WATANABE, K.; MORINAGA, Y.; YOSHINAGA, F. (**1998**) ACETYLATION OF BACTERIAL CELLULOSE: PREPARATION OF CELLULOSE ACETATE HAVING A HIGH DEGREE OF POLYMERIZATION. *BIOSCI. BIOTECHNOL. BIOCHEM.* 62(7), 1451-1454.

TAYLOR, A.W.; LOVELOCK, K.R.J.; DEYKO, A.; LICENCE, P. JONES, R.G. (**2010**) HIGH VACUUM DISTILLATION OF IONIC LIQUIDS AND SEPARATION OF IONIC LIQUID MIXTURES. *PHYS. CHEM. CHEM. PHYS.* 12, 1772-1783.

VARANASI, S.; SHALL, A.C.; DADO, P.A.; ANDERSON, J.; RAO, K.; PARIPATI, P. (**2008**) BIOMASS PRETREATMENT. WO 2008/11291A2.

WALDEN, P. (**1914**) MOLECULAR WEIGHTS AND ELECTRICAL CONDUCTIVITY OF SEVERAL FUSED SALTS. BULLETIN DE L'ACADEMIE IMPERIALE DES SCIENCES DE ST.-PETERSBOURG, 405-422.

WASSERSCHEID, P. (**2006**) VOLATILE TIMES FOR IONIC LIQUIDS. *NATURE* 439, 797.

WEINGÄRTNER, H. (**2008**) UNDERSTANDING IONIC LIQUIDS AT THE MOLECULAR LEVEL: FACTS, PROBLEMS, AND CONTROVERSIES. *ANGEW. CHEM. INT. ED.* 47, 654-670.

WELTON, T. (**2003**) POLARITY. IN: WASSERSCHEID, P.; WELTON, T. (EDS.) IONIC LIQUIDS IN SYNTHESIS. WILEY-VCH, WEINHEIM

WERPY, T.; PEDERSEN, G. (**2005**) TOP VALUE ADDED CHEMICALS FROM BIOMASS, VOL. 1. US DEPARTMENT OF ENERGY HTTP://WWW1.EERE.ENERGY.GOV/BIOMASS/PDFS/35523.PDF

WILKES, J.S.; LEVINSKY, J.A.; WILSON, R.A.; HUSSEY, C.L. (**1982**) DIALKYLIMIDAZOLIUM CHLOROALUMINATE MELTS: A NEW CLASS OF ROOM-TEMPERATURE IONIC LIQUIDS FOR ELECTROCHEMISTRY, SPECTRSOCOPY AND SYNTHESIS. *INORG. CHEM.* 21, 1263.

WILKES, J.S.; ZAWOROTKO, M.J. (**1992**) AIR AND WATER STABLE 1-ETHYL-3-METHYLIMIDAZOLIUM BASED IONIC LIQUIDS. *J. CHEM. SOC., CHEM. COMMUN.* 965-967.

WILKES, J.S. (**2002**) A SHORT HISTORY OF IONIC LIQUIDS – FROM MOLTEN SALTS TO NEOTERIC SOLVENTS. *GREEN CHEM.*, 4, 73-80.

WILKES, J. S. (**2003**) INTRODUCTION. IN: WASSERSCHEID, P.; WELTON, T. (EDS.) IONIC LIQUIDS IN SYNTHESIS. WILEY-VCH, WEINHEIM

WU, J.; ZHANG, J.; ZHANG, H.; HE, J.; REN, Q.; GUO, M. (**2004**) HOMOGENOUS ACETYLATION OF CELLULOSE IN A NEW IONIC LIQUID. *BIOMACROMOL.* 5, 266-268.

XIE, H.; KING, A.; KILPELAINEN, I.; GRANSTROM, M.; ARGYROPOULOS, D.S. (**2007**) THOROUGH CHEMICAL MODIFICATION OF WOOD-BASED LIGNOCELLULOSIC MATERIALS IN IONIC LIQUIDS. *BIOMACROMOL.* 8, 3740-3748.

YAMAMOTO, H.; HORII, F. (**1993**) CP/MAS 13C NMR ANALYSIS OF THE CRYSTAL TRANSFORMATION INDUCED FOR *VALONIA* CELLULOSE BY ANNEALING AT HIGH TEMPERATURES. *MACROMOLECULES*, 26, 1313-1317.

YELLE, D.J.; RALPH, J.; FRIHART, C.R. (**2006**) INVESTIGATION INTO HOW WOOD CELL WALLS INTERACT WITH SYNTHETIC ADHESIVES USING HIGH-RESOLUTION SOLUTION-STATE NMR SPECTRSOCOPY. ABSTRACT OF PAPERS, 231ST ACS NATIONAL MEETING, ATLANTA, GA, UNITED STATES, MARCH 26-30.

YOKE, J.T.; WEISS, J.F.; TOLLIN, G. (**1963**) REACTIONS OF TRIETHYLAMINE WITH COPPER (I) AND COPPER(II) HALIDES. *INORG. CHEM.* 2, 1210-1212.

ZAVREL, M.; BROSS, D.; FUNKE, M.; BÜCHS, J.; SPIESS, A.C. (**2009**) HIGH-THROUPUT SCREENING FOR IONIC LIQUIDS DISSOLVING (LIGNO-)CELLULOSE. *BIORESOURCE TECHNOL.* 100, 2580-2587.

ZENG, M.; MOSIER, N.S.; HUANG, C.-P.; SHERMAN, D.M.; LADISCH, M.R. (**2007**) MICROSCOPIC EXAMINATION OF CHANGES OF PLANT CELL STRUCTURE IN CORN STOVER DUE TO HOT WATER PRETREATMENT AND ENZYMATIC HYDROLYSIS. *BIOTECHNOL. BIOENG.* 97(2), 265-278.

ZHAI, W.; CHEN, H.Z.; MA, R.Y. (**2007**) STRUCTURAL CHARACTERISTICS OF CELLULOSE AFTER DISSOLUTION AND REGENERATION FROM THE IONIC LIQUID [bmim]Cl. BEIJING HUAGONG DAXUE XUEBAO. ZIRAN KEXUEBAN 34(2), 138-141.

ZHANG, J.; ZHANG, H.; WU, J.; ZHANG, J.; HE, J. (**2010**) NMR SPECTROSCOPIC STUDIES ON CELLOBIOSE SOLVATION IN EMIMAC AIMED TO UNDERSTAND THE DISSOLUTION MECHANISM OF CELLULOSE IN IONIC LIQUID. *PHYS. CHEM. CHEM. PHYS.* 12, 1941-1947.

ZHU, S.; WU, Y.; CHEN, Q.; YU, Z.; WANG, C.; JIN, S.; DINGA, Y.; WU, G. (**2006**) DISSOLUTION OF CELLULOSE WITH IONIC LIQUIDS AND ITS APPLICATION: A MINI-REVIEW. *GREEN CHEM.* 8, 325-327.

5. PUBLICATIONS

PUBLISHED

1. **Schrems, M.**; Ebner, G.; Liebner, F.; Becker, E.; Potthast, A.; Rosenau, T. (**2010**) Side reactions in the system cellulose/1-alkyl-3-methyl-imidazolium ionic liquid. In: Liebert, T.; Heinze, T.; Edgars, K. (Eds.), Cellulose Solvents: For Analysis, Shaping and Chemical Modification. 149-164; American Chemical Society, Washington, D.C.; ISBN 9780841200067

2. **Schrems, M.**; Vejdovszky, P.; Zeilinger, M.; Bednarik, S.; Haimer, E.; Liebner, F.; Rosenau, T.; Potthast, A. (**2011**) Organosolv revisited – biomass valorization with new perspectives. Conference Proceedings, 11th AIChE Spring Meeting & 7th Global Congress on Process Safety, Chicago, IL, United States, March 13-17, 2011 (*not specified*)

3. Liebner, F.; Pour, G.; Klinger, K.; **Schrems, M**.; Tyhoda, L.; Potthast, A.; Rosenau, T. (**2011**) Ammonoxidation meets biorefinery: A promising approach for valorizing ligneous materials and combating global desertification. Abstracts of Papers, 241st ACS National Meeting & Exposition, Anaheim, CA, United States, March 27-31, 2011. (*not specified*)

4. **Schrems, M.**; Brandt, A.; Welton, T.; Liebner, F.; Rosenau, T.; Potthast, A. (**2011**) Ionic liquids as media for biomass processing: opportunities and restrictions. *Holzforschung* 65(4), 527-533.

SUBMITTED

5. **Schrems, M.**; Brandt, A.; Hallett, J.P.; Murphy, R.J.; Potthast, A.; Ray, M.; Rosenau, T.; Welton, T. (**2011**) Ionic Liquid Pretreatment of Pine Wood Chips for Reduced Energy Input during Grinding. Manuscript submitted to Green Chem.

IN PREPARATION

6. **Schrems, M.**; Liebner, F.; Betz, M.; Zeilinger, M.; Rosenau, T.; Potthast, A. (**2011**) Understanding the impact of super critical carbon dioxide on the delignification mechanism during organosolv pulping. Manuscript in preparation for J. Wood Chem. Technol.

6. APPENDIX

A. PUBLICATIONS

1. *Schrems, M.; Ebner, G.; Liebner, F.; Becker, E.; Potthast, A.; Rosenau, T. (2010) Side reactions in the system cellulose/1-alkyl-3-methylimidazolium ionic liquid. In: Liebert, T.; Heinze, T.; Edgars, K. (Eds.), Cellulose Solvents: For Analysis, Shaping and Chemical Modification. 149-164; American Chemical Society, Washington, D.C.; ISBN 9780841200067*

2. *Schrems, M.; Brandt, A.; Welton, T.; Liebner, F.; Rosenau, T.; Potthast, A. (2011) Ionic liquids as media for biomass processing: opportunities and restrictions. Holzforschung 65(4), 527-533.*

3. *Schrems, M.; Liebner, F.; Betz, M.; Zeilinger, M.; Rosenau, T.; Potthast, A. (2011) Understanding the impact of super critical carbon dioxide on the delignification mechanism during organosolv pulping – a model substance study. Manuscript in preparation for J. Wood. Chem. Technol.*

4. *Schrems, M.; Brandt, A.; Hallett, J.P.; Murphy, R.J.; Potthast, A.; Ray, M.; Rosenau, T.; Welton, T. (2011) Ionic Liquid Pretreatment of Pine Wood Chips for Reduced Energy Input during Grinding. Manuscript submitted to Green Chem.*

B. CURRICULUM VITAE

Side Reactions in the System Cellulose/1-Alkyl-3-methyl-imidazolium Ionic Liquid

Michael Schrems[1], Gerald Ebner[1], Falk Liebner[1], Ernst Becker[2], Antje Potthast[1] and Thomas Rosenau[1,*]

[1]University of Natural Resources and Applied Life Sciences Vienna (BOKU), Department of Chemistry and Christian Doppler Laboratory "Advanced Cellulose Chemistry and Analytics", Muthgasse 18, A-1190 Vienna, Austria
[2]Blue Globe Energy GmbH, Willy-Brandt-Platz 6, D-68161 Mannheim, Germany
*thomas.rosenau@boku.ac.at

In solutions of cellulose in 1-alkyl-3-methyl-imidazolium ILs, both the ionic liquid and the cellulose are evidently not inert. Side reactions can be distinguished according to whether they involve the cation or the anion of the ionic liquid or just autodegradation products of the IL. Ionic liquids with 1-alkyl-3-methyl-imidazolium cations react at C-2 with cellulose at its reducing end (and, if present, other aldehyde functionalities along the chain), forming a carbon-carbon bond. The reaction is strongly catalyzed by bases, so that commonly present impurities in ILs, such as their thermal degradation products, promote this reaction. These thermal degradation products are mainly imidazole, *N*-alkylimidazole, *N*-methylimidazole and methylene-bridged dimers. Side reactions of ILs anions are more divers and depend on the respective reaction system. Acetate as the IL anion is generally unsuitable for esterifications by acylating agents (halides, anhydrides), both organic and inorganic ones, for methylations (alkyl halides, dialkyl sulfate), or for silylations (trimethylsilyl halides), since the reagents coreact with the IL anion rather than with the cellulosic hydroxyls. Chloride anions in the IL cannot be used for alkylations (alkyl halides, dialkyl sulfate) or oxidations (NMMO, periodate).

Introduction

Within the past several years, ionic liquids (ILs) have attracted much interest in cellulose chemistry as dissolution (*1*, *2*) and derivatization media (*3–6*). There is also industrial interest in the use of ILs for production of cellulosic fibers and shaped cellulosics in general (*7–9*). The far-reaching non-reactivity and good solvent properties of ILs seems to render them competitors to the Lyocell technology which is based on *N*-methylmorpholine-*N*-oxide monohydrate (NMMO/H_2O). Although this solvent is also able to dissolve celluloses directly, it needs elevated temperatures, is a rather strong oxidant and tends to be quite unstable. Those disadvantages could, in principle, be overcome by ILs which in addition are able to dissolve larger percentages of cellulose compared to NMMO, but the chemical and technological research towards a large-scale application is still in a juvenile state. Especially 1-butyl-3-methyl-imidazolium (BMIM) and 1-ethyl-3-methyl-imidazolium (EMIM), both as acetate or chloride (**1** – **4**, Scheme 1), have found wide utilization in cellulose and polysaccharide chemistry.

It has been realized that the integrity of the cellulose chain during dissolution and derivatization in ILs is largely dependent on the purity of these solvents and of the absence of IL-derived byproducts. We recently observed that cellulose after dissolution in imidazolium-based ILs and re-precipitation showed less fluorescence with the carbonyl-selective fluorescence label CCOA (*10*) than the starting cellulose labeled directly. The carbonyl groups (*e.g.* the reducing ends) seemed to be somehow "inactivated" towards labeling, possibly indicating a reaction between the ILs and carbonyl groups of the cellulose. Such carbonyls are present in the form of a hemiacetal at the reducing end of the cellulose chain, and as keto (C-2, C-3) or aldehyde (C-6) groups along the cellulose chain, which are the result of random oxidation during cellulose processing (pulping, bleaching) and aging.

In the literature, the reactivity of C-2 in imidazolium moieties finds ample coverage (*11*). In particular, there is one report on side reactions of imidazolium-based ionic liquids in base-catalyzed Baylis–Hillman reactions (*12*), where it was shown that 1-butyl-3-methylimidazolium (BMIM) ionic liquids participate in the reaction with aldehyde groups, being deprotonated at C-2 to give species capable of reacting with electrophiles, such as benzaldehyde. Also the acetylating action of BMIM acetate onto cellulose has been demonstrated recently (*13*) showing that also the anion part of the IL can be involved in side reactions. In this paper we would like to communicate that 1-alkyl-3-methylimidazolium ILs react with aldose carbohydrate model compounds and with cellulose, demonstrating that neither the heterocyclic cation nor the anion of ILs commonly used in cellulose chemistry (EMIM acetate and chloride, BMIM acetate and chloride) behave in an inert manner (towards cellulose or coreactants), and that thermal degradation products of the ILs promote some of these side reactions.

Scheme 1. Chemical structure of the ionic liquids 1-butyl-3-methyl-imidazolium acetate (BMIM-OAc, **1**), 1-butyl-3-methyl-imidazolium chloride (BMIM-Cl, **2**), 1-ethyl-3-methyl-imidazolium acetate (EMIM-OAc, **3**), and 1-ethyl-3-methyl-imidazolium chloride (EMIM-Cl, **4**).
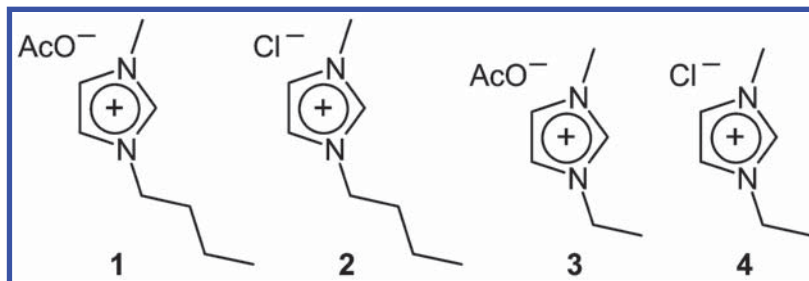
Scheme 2. Reaction of BMIM-OAc (**1**) with 1-^{13}C-D-glucopyranose (**5**) to the diastereomeric addition products **6a** and **6b**.
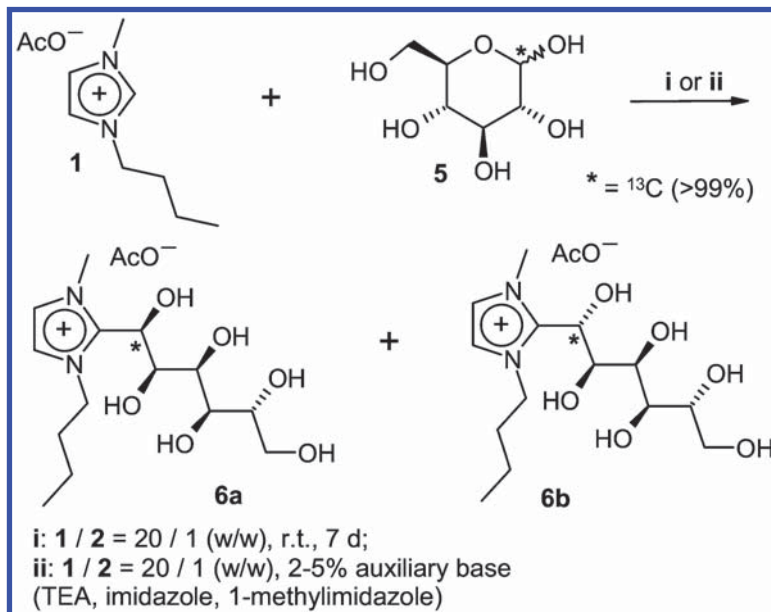
Results and Discussion

Reactions of the IL Cations

To simulate the reactivity of the reducing end of celluloses we used D-glucose as a very simple, but well fitting model compound. It is present as natural mixture of α- and β-D-glucopyranoside. A glucose with a ^{13}C-label at position C-1 (>99%, **5**) allowed following the reaction at the reducing end more

specifically. The intensity gain by roughly the factor 100 in ^{13}C NMR would allow to reliably detect even minor side reactions at this position: if 10% of the glucopyranose in a 10% solution in 1-alkyl-3-methylimidazolium ILs would form a byproduct, its corresponding resonance would still be in the same intensity order as those of the solvent. Figure 1 shows the ^{13}C NMR spectrum of the 1-butyl-3-methylimidazolium acetate (**1**, Fig. 1A), and of 5% 1-^{13}C-D-glucose (**5**) in this IL immediately after dissolution (Fig. 1B). The resonances at approx. 99 ppm and 93 ppm correspond to the *β*-D-glucopyranose and *α*-D-glucopyranose forms, respectively [The small resonances between 60 and 80 ppm belong to the (non-labeled) peaks of the glucose atoms C-2 to C-6, the peaks at 97 and 105 ppm to the (labeled) C-1 of the glucofuranosides in equlibrium concentration (<0.5%)]. After 7 days of storage under inert atmosphere at room temperature, clearly two new signals (at approx. 65 ppm and 67 ppm) had developed (Fig. 1C), which originate from the addition products **6a** and **6b**, formed by electrophilic attack of C-2 of the imidazolium at the anomeric carbon of **5** (Scheme 2) [The assignment of the two shifts to the two diastereomeric products was based on the calculated NMR shifts (Spartan 2004, HF, 6-311G(d,p)) with the resonance of the former C-1 appearing at higher field for **6a**].

The same outcome was observed already after 2h in the presence of catalytic amounts of triethylamine (TEA, additional small resonances at 11.7 ppm and 45.7 ppm) at r.t., see Fig. 1D. In both cases, about 15% of the glucopyranose were converted into the corresponding addition product by reaction with BMIM-OAc (**1**). It was evident that the IL reacted with the glucopyranose both at longer reaction times and upon base catalysis.

The same reaction was confirmed for other aldopyranoses, such as mannose, xylose, cellobiose and cellotriose. The reaction rates, as roughly approximated by ^{13}C NMR using 2-^{13}C-BMIM-OAc (*14*) (**1***, see also Scheme 3) were very similar in all cases, and also the catalytic effect of bases was always provable. Assuming similar reactions to occur under similar conditions with aldehyde/hemiacetal functions in cellulose, we faced the analytical problem that the amount of IL bound to cellulose (**7**) would be rather small. In the case of an IL cation reacting with glucose, both moieties are present in a 1:1 ratio in the product. At a cellulose DP (degree of polymerization, number of anhydroglucose units) of 500, there is per 500 glucopyranose units just one reducing glucopyranose end available for reaction with the IL, giving a 500:1 ratio (provided that indeed all reducing ends would react). Such a small amount of derivatized reducing ends is impossible to track down by NMR and is also within the error limits of microanalysis (N content). However, when we used isotopically labeled ionic liquid (2-^{13}C-BMIM-OAc, **1***), the NMR resonance intensity of the co-reacting C-2 in the IL is multiplied by approx. 100, and thus approaches the detectable range. Indeed, a cellulose dissolved in **1*** for 7 d, then precipitated, and finally measured by NMR in DMAc-d$_9$/LiCl (2.5%, w/w) shows a weak but clearly discernible resonance at 147.8 ppm, corresponding to C-2 in the imidazolium moieties of the endwise-derivatized cellulose (**8**), see Scheme 3. The same outcome was observed when the cellulose was dissolved in **1*** in the presence of 3% TEA or imidazole, precipitated and re-dissolved for NMR measurement. C-2 in **1** (and **1***) resonates (^{13}C NMR) at 137 ppm. This resonance was absent
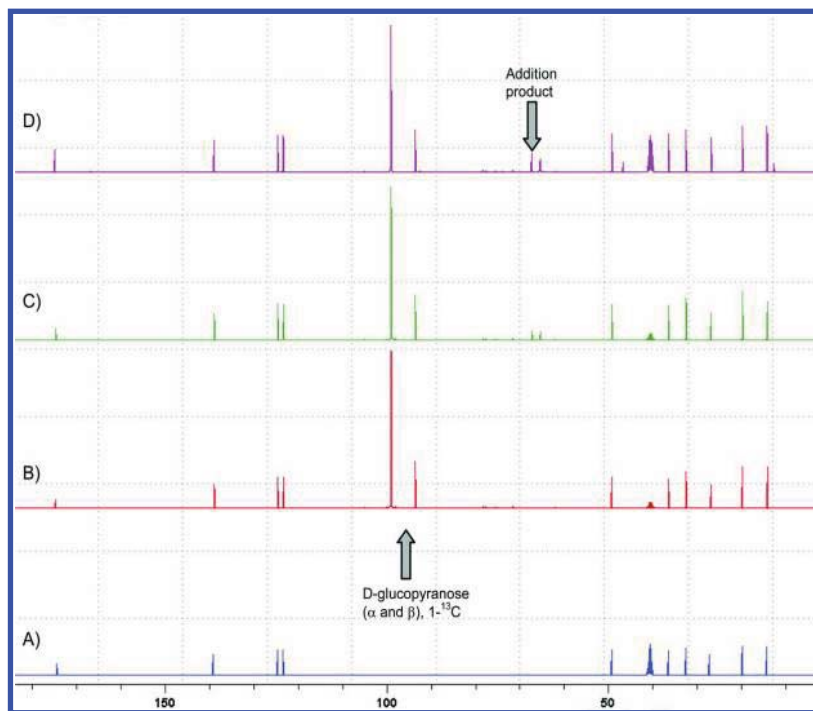
*Figure 1. ^{13}C NMR spectra (ppm). A) BMIM-OAc (1); B) BMIM-OAc and 5%
1-^{13}C-D-glucose (5, 5%, w/w), spectrum acquired immediately after dissolution;
C) composition as in B), measured after 7 d at r.t., D) BMIM-OAc, 5%
1-^{13}C-D-glucose (5, 5%, w/w), and 3% TEA (w/w), spectrum acquired after 2 h.*

in **6a/b** and in the precipitated derivatized "BMIM-cellulose" **8**, and just the
C-2 resonance at 147.8 ppm was present. In the case of using ^{13}C-perlabeled
cellulose (**9**) (*15*) the direct carbon-carbon linkage between the reducing end
of cellulose and C-2 of the IL heterocycle in the labeled "BMIM-cellulose" **10**
became evident by the direct homonuclear coupling of these two carbons with
a $^1J_{C,C}$ of 38 Hz, which split the IL-C-2 resonance into a doublet (d, 148 ppm,
coupling with cellulose-C-1, *i.e.* the reducing end) and the signal of the reducing
end of cellulose into a doublet of doublets (dd, 68.5 ppm, coupling with IL-C-2,
$^1J_{C,C}$ = 38 Hz, and with C-2 of cellulose, $^1J_{C,C}$ = 19 Hz), see Scheme 3.

Preliminary experiments have shown that addition of strong bases to the
addition products between glucose (or other aldoses or cellulose, respectively)
and IL apparently caused a reversal of the addition reaction (a retro-aldol
type cleavage). This is in line with observations on the reversible addition
of 1-butyl-3-methyl-imidazolium IL to benzaldehyde (*9*). This finding,
which is current under further scrutiny, implies that cellulose derivatized in
1-alkyl-3-methyl-imidazolium ILs becomes derivatized at the reducing end
according to Figure 3, but might lose the IL moiety over time in a reversal of the
addition process. Due to the negligible vapor pressure of the ILs, the released IL,
although present in minute amounts only, cannot leave the cellulosic material and

153

*Scheme 3. Reaction of ^{13}C-labeled 1-butyl-3-methylimidazolium IL (**1***) with cellulose (**7**) at its reducing end to the "BMIM-cellulose" derivative **8** and with ^{13}C-perlabeled cellulose **9** to "labeled BMIM-cellulose" **10**, both products having ^{13}C NMR-detectable cellulose-IL linkages.*
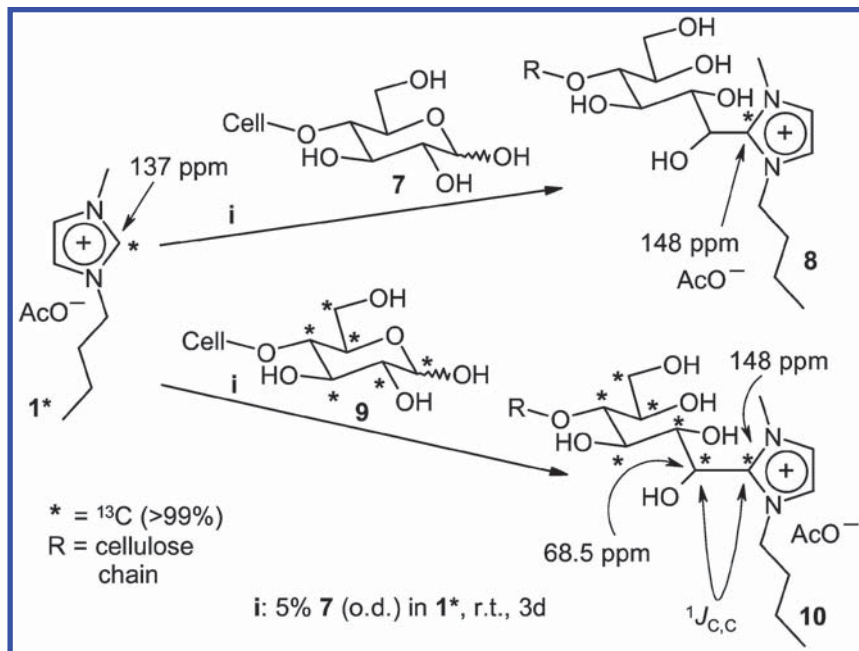

will accumulate there, which should be kept in mind as a possible problem for medical and physiological application scenarios of IL-processed cellulosics.

To further prove the derivatization of cellulose by ILs based on 1-alkyl-3-methyl-imidazolium, we used 1-(2-naphthylmethyl)-3-methyl-imidazolium acetate (NapMIM, **11**) instead of BMIM-OAc (**1**). Having otherwise similar reactivity, **11** carries a UV- and fluorescence-active naphthyl moiety, which can be used to report the IL moiety in derivatives. While the reaction product of BMIM with cellulose has no fluorescence, the analogous NapMIM-cellulose derivative (**12**) is strongly fluorescent (Scheme 4). This property can be used to verify by size exclusion chromatography (SEC) (For details of the GPC system used see part b of ref (*8*)) whether indeed an IL-based moiety is attached to cellulose after dissolution of cellulose in this ionic liquid. In the case of IL being only adsorbed or adherent to cellulose, fluorescence would occur only in the SEC exclusion peak (long retention times), but not along the molecular weight distribution of the cellulose. If, on the contrary, the IL was covalently bound to the cellulose, there would be a discernible fluorescence signal also along the molecular weight distribution, indicating the endwise derivatization of the cellulose chains by the IL.

Indeed, as given in Figure 2, the cellulose was derivatized by NapMIM (**11**) as seen by the distinct fluorescence signal of this compound. The cellulose was dissolved in the IL for 3d, subsequently re-precipitated and re-dissolved for the

Scheme 4. Reaction of (2-naphthylmethyl)methyl-imidazolium IL (NapMIM-OAc, 11) with cellulose at its reducing end to fluorescent derivative 12, that is detectable with fluorescence-SEC.
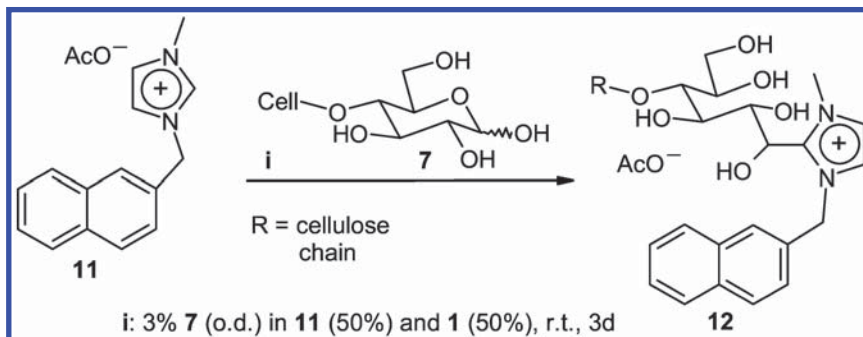
Scheme 5. Thermal degradation products of B(E)MIM ionic liquids upon thermal stress (200°C for 24 h, closed vessel, inert atmosphere).
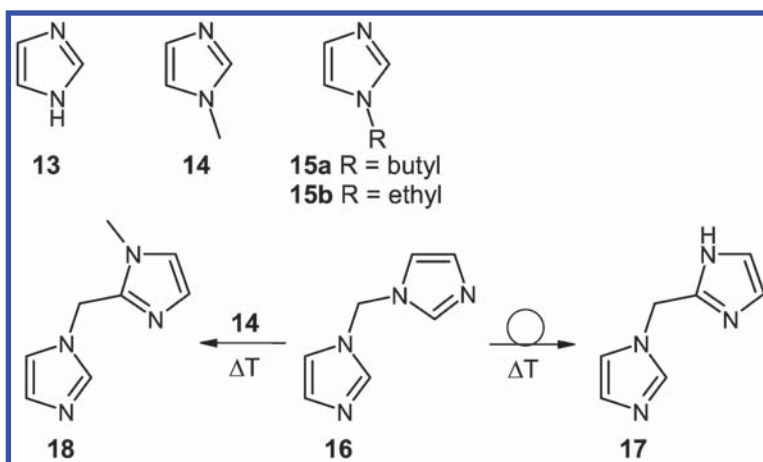
SEC measurement. Similar results were obtained also after only 8h of dissolution time. Thus, already after such relatively short times in IL solution, the cellulose reacted with the 1-alkyl-3-methyl-imidazolium IL, which caused a derivatization at the reducing end as shown in Schemes 3 and 4. The fact that the fluorescence signal follows the molecular weight distribution (MWD) of the cellulose quite closely in shape moreover demonstrated that this endwise derivatization occurred more or less independent of the chain length: derivatization proceeded in all molecular weight regions equally well, and no region was suppressed or preferred.

Thermal Degradation of ILs

It has been recognized frequently that reactions in ILs – also reactions of cellulose – are dependent with regard to rate, yield, and side processes on the
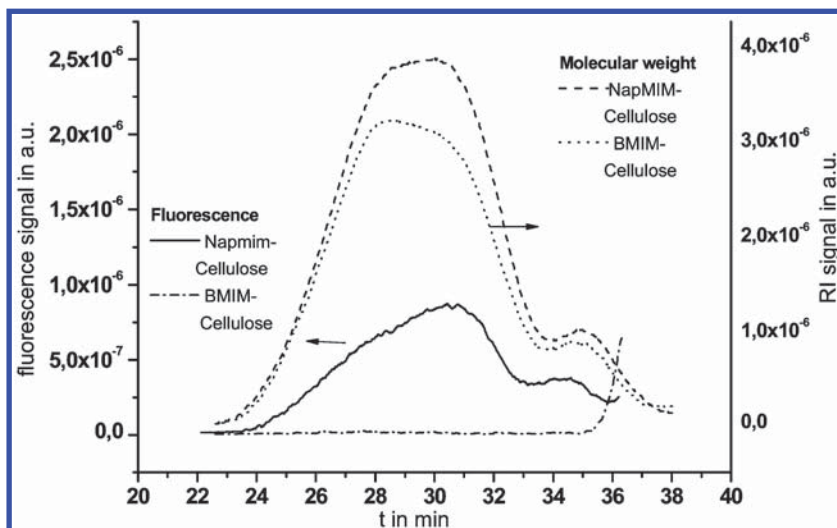
*Figure 2. Molecular weight distributions (right y-axis) and fluorescence signals
(left y-axis) of BMIM-derivatized (**8**) and NapMIM-derivatized (**12**) cellulose.
No fluorescence was detectable in the case of BMIM (dash-dot line), whereas
cellulose dissolved in NapMIM gave a clear fluorescence signal over the whole
range of the molecular weight (solid line). The shape of the molecular weight
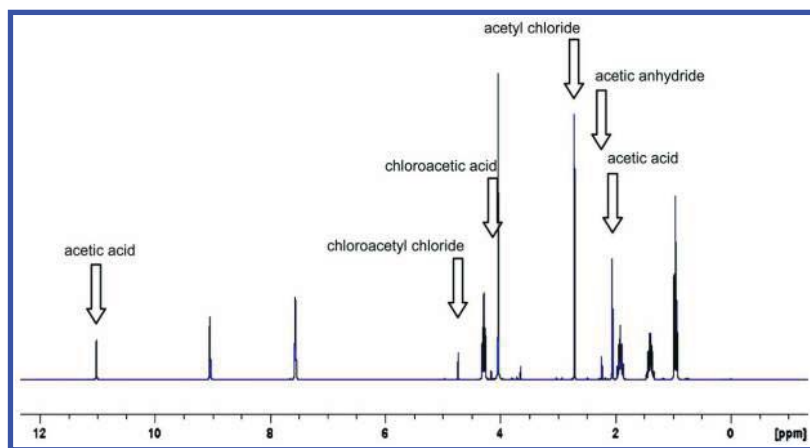distribution did not change significantly upon reaction with either IL (cf.
refractive index (RI) signal).*

*Figure 3. ^{1}H NMR spectrum (ppm scale) of a mixture of BMIM-OAc (**1**) and
sulfuryl chloride (molar ratio 2:1), acquired 15 min after mixing. Besides the
evident major peaks of acetyl chloride (**22**) and acetic anhydride (**23**), some
minor byproducts (chloroacetic acid, chloroacetyl chloride) are visible.*

purity and "freshness" of the ILs. This effect is also related to the recyclability
of ILs, with byproducts possibly accumulating and affecting the outcome of
the processes. The recyclability is, however, not the subject of this study. We

were focusing instead on the thermal stability of the ILs **1 – 4**, starting from the observation that the side reaction with glucose (Scheme 2) and cellulose (Scheme 3) proceeded clearly faster in ILs that were heated for some time, whereas the reaction was much slower in freshly purified (extracted, silica gel filtered) ILs. This indicated the formation of basic compounds – as the above side reaction is catalyzed by bases – which were highly likely derived from the heterocyclic IL cation. Applying extraction in combination with adsorption to acidic alumina (Brockmann grade II), we were able to isolate the degradation products shown in Scheme 5 (*16*). Thermal degradation produces imidazole (**13**), *N*-methylimidazole (**14**), *N*-alkylimidazole (**15a**, alkyl = butyl, from **1** and **2**; **15b**, alkyl = ethyl, from **3** and **4**). Apart from these compounds, dimeric compounds (**16 – 18**) were found, in which the methyl group was converted into a methylene bridge. Interestingly, the former 1-alkyl group (butyl or ethyl) was not found in any of the dimeric compounds, although the reason for this behavior cannot be conclusively accounted for at the moment. Bis(1-imidazolyl)methane (**16**) was shown to be a precursor of 2-(imidazol-1-ylmethyl)-imidazole (**17**): under thermal treatment (T > 150°C) the former is rearranged into the latter. The preliminary elimination product, an *N*-(methylene)imidazolium cation being a Mannich intermediate, performs an electrophilic attack at C-2 of imidazole. Product **17** can be regarded as a Mannich base formed from imidazole and formaldehyde, the C_1-bridging unit being formed from the former *N*-methyl group. Analogously, attack of the *N*-(methylene)imidazolium at C-2 of *N*-methylimidazole (instead of imidazole) produces the degradation product 2-(imidazol-1-ylmethyl)-1-methyl-imidazole (**18**). Carried out in a sealed autoclave, thermal treatment of **1 – 4** at 200°C for 24 h generated 0.08%, 0.02%, 0.05% and 0.006% of net degradation products, indicating the BMIM derivatives to be slightly less stable compared to the EMIM counterparts, and the acetate anions being slightly promotive to degradation as compared to chloride, possibly due to their higher basicity.

It is important that the thermal degradation products (**13 – 18**) carry secondary, tertiary and aromatic amine functionalities and are thus all relatively strong bases, which explains their promoting effect on the above reaction between 1-alkyl-3-methyl-imidazolium and the reducing ends of aldopyranoses/cellulose (Schemes 2 and 3). The degradation products will have accumulated in ILs after long thermal stress, so that those ILs are much more likely to undergo side reactions with cellulose than freshly purified ones. Thus, removal of such degradation impurities (and of bases in general) is an easy preventive measure to minimize such side reactions. All thermal degradation products shown in Scheme 5 have been unambiguously identified by their NMR (^{1}H, ^{13}C) and MS data, also in comparison to authentic samples that were either commercially available (**13 – 15**) or synthesized according to standard protocols (**16 – 18**).

Reactions of the IL Anions

The anions of BMIM/EMIM-type ionic liquids can vary widely. Whereas in earlier days of IL research some complex anions, such as for instance PF_6^-, $AlCl_4^-$ or BF_4^-, were more common, nowadays mainly acetate and chloride are

*Scheme 6. Side reactions of BMIM-OAc (**1**) in esterifications with carboxylic acid chlorides (**19**) or anhydrides (**20**) causing formation of strongly acetylating agents (**21 – 23**) and eventually cellulose acetylation. The same generation of the strongly acetylating species acetyl chloride (**22**) and acetic anhydride (**23**) from the IL counter-anion acetate occurs as well with inorganic chlorides and anhydrides, see Figure 3 and text.*
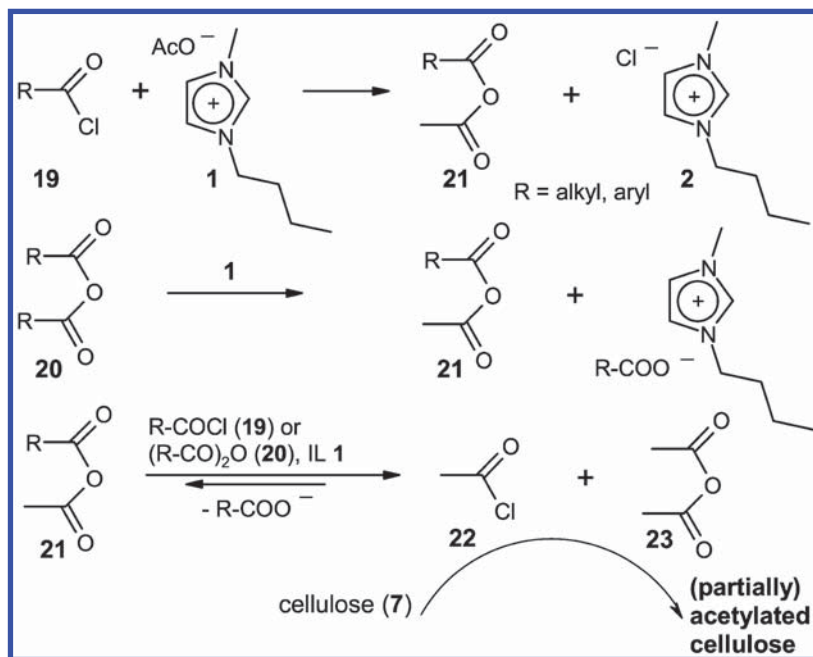
used, especially in cellulose chemistry and processing. Also the anions in ILs – chloride and acetate in this study – are not inert with regard to cellulose integrity. While the cation (1-alkyl-3-methyl-imidazolium) reacts directly with the solute cellulose, the reactions of the anions do not occur directly with cellulose, but primarily with reagents that are added for cellulose derivatization. This way, intermediates are formed which, in turn, might then cause side reactions with cellulose. In the following, examples for such reactions of IL anions are given. It should be mentioned that – while the reaction of cellulose with the cations was quite unexpected – some of the reactions of the IL anions were more evident and followed quite obviously from general chemistry.

A general case for IL anion side reactions is the attempted esterification of cellulose in BMIM-OAc (**1**) with organic or inorganic acid chlorides (**19**) or anhydrides (**20**), which does not give the expected esters of the carboxylic acid, the first example of this behavior being described in (*10*). Instead, cellulose acetate or mixed esters are formed. Both reagents **19** and **20** form reactive intermediates with the acetate anion of the IL: the mixed carboxylic acetic anhydride (**21**), acetyl chloride (**22**), and acetic anhydride (**23**), see Figure 3 and Scheme 6. The same reaction occurs with inorganic acid chlorides, *e.g.* sulfuryl

Scheme 7. Side reactions of EMIM/BMIM acetates and chlorides in methylations of cellulose with methyl iodide (24) or dimethyl sulfate (25) causing consumption of the methylating agent by formation of methyl chloride (26) which is volatile and in addition a much weaker methylating agent, or methyl acetate (27), respectively, which has no methylating activity.
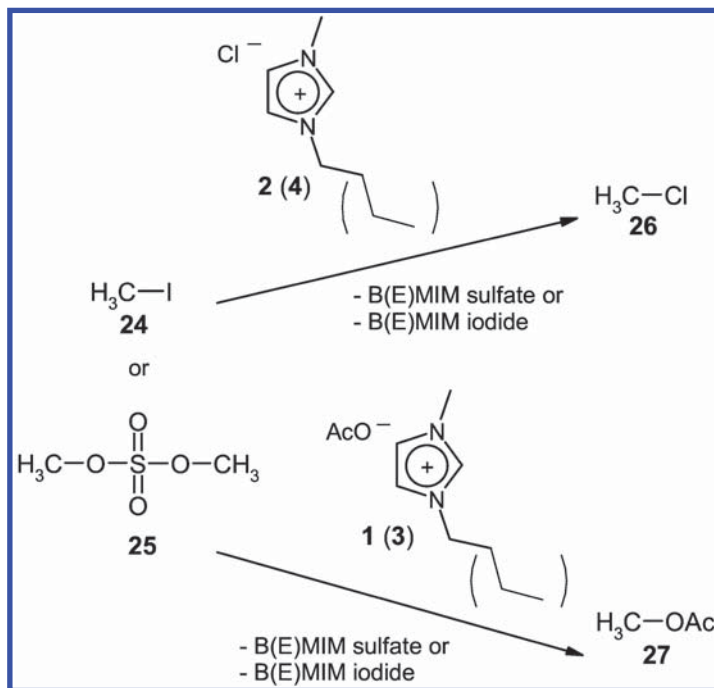
chloride, thionyl chloride, phosphoryl chloride, or anhydrides, *e.g.* phosphorous pentoxide, sulfur trioxide and its complexes (Figure 3).

Also in these cases acetyl chloride (**22**) and acetic anhydride (**23**) are generated, which both cause cellulose acetylation as a side reaction. These acetylating compounds, their occurrence being experimentally confirmed by NMR (Figure 3) and GC/MS detection, are formed according to dynamic equilibria, independent of the presence of cellulose in the reaction system. However, in the presence of cellulose, the reactive intermediates are consumed by acetylation of cellulose and are continuously regenerated as long as acid chloride/anhydride as the starting material is present. Simultaneously, acetate as the IL anion is replaced by the corresponding carboxylate/acid anion. As a consequence, BMIM-OAc (**1**) and EMIM-OAc (**3**) cannot be used as solvents for esterification of cellulose with organic and inorganic acids, if the corresponding acid chlorides or anhydrides are to be used as the acylating agents. In these cases, acetylation of cellulose will inevitably occur as side reaction or even as the main process. By analogy to the acetate anion, also any other carboxylate as the BMIM counter-anion (as e.g. in BMIM benzoate or BMIM propionate) will cause formation of the corresponding cellulose carboxylic acid ester (benzoate or
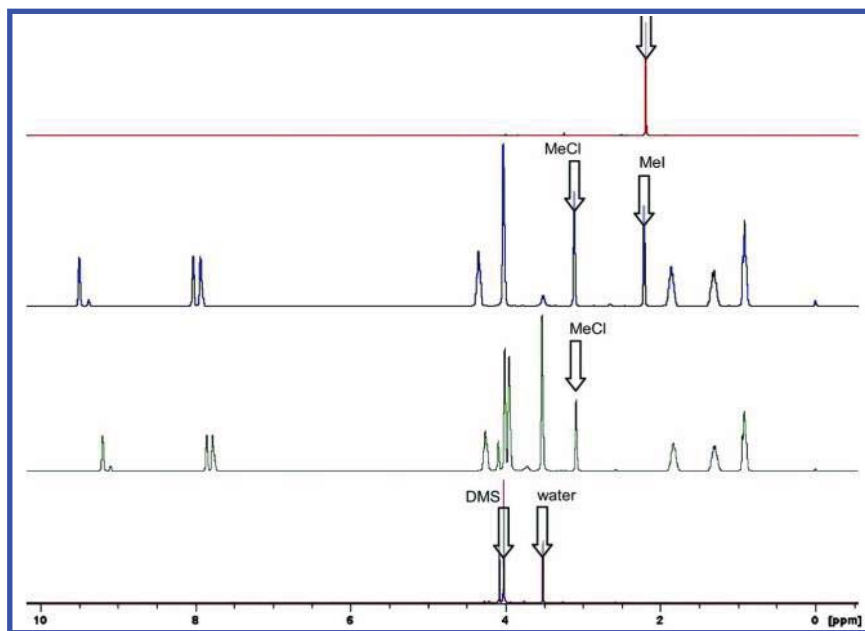
*Figure 4. ^{1}H NMR spectra (ppm scale). Upper trace: methyl iodide (**24**), second upper trace: a mixture of BMIM chloride (**2**) and methyl iodide (**24**), acquired 15 min after mixing, second lower trace: a mixture of BMIM chloride (**2**) and dimethyl sulfate (DMS, **25**) acquired 15 min after mixing, lower trace: dimethyl sulfate (**25**). In the two middle spectra, the formation of methyl chloride (**26**) from the methylating agents is evident.*

propionate, respectively) if an esterification of cellulose with organic/inorganic halides or anhydrides in this system is attempted.

Another side reaction of IL anions occurs if methylation of cellulose is carried out in BMIM chloride (**2**) or EMIM chloride (**4**), applying e.g. methyl iodide (**24**) or dimethyl sulfate (**25**) as methylating agents under alkaline conditions (Scheme 7).

In BMIM/EMIM chloride, both methylating agents are converted into methyl chloride (**26**) by nucleophilic substitution involving the chloride anion of the IL, which is replaced by iodide or (methyl)sulfate, respectively (see Scheme 7 and Figure 4). The methyl chloride (**26**) partly leaves the reaction system, as it is a volatile gaseous compound – but even dissolved portions react by 2 to 3 orders of magnitude slower than Me-I under otherwise identical conditions. If BMIM/EMIM acetates (**1**, **3**) are used for methylations, the main reaction is the conversion of the anion into methyl acetate (acetic acid methyl ester, **27**) rather than methylation of the (cellulosic) substrate (Scheme 7). Thus, neither 1-alkyl-3-methylimidazolium chlorides (**2**, **4**) nor 1-alkyl-3-methylimidazolium acetates (**1**, **3**) can be used in methylation reactions of celluloses, since the commonly used methylating agents are either lost or at least "inactivated" by side reactions with the chloride/acetate anion of the IL solvent.

Scheme 8. Side reactions of EMIM/BMIM acetates in trimethylsilylations of cellulose with TMS reagents (28, see text), causing formation of trimethylsilyl acetate (29), which is volatile and has no trimethylsilylating activity.
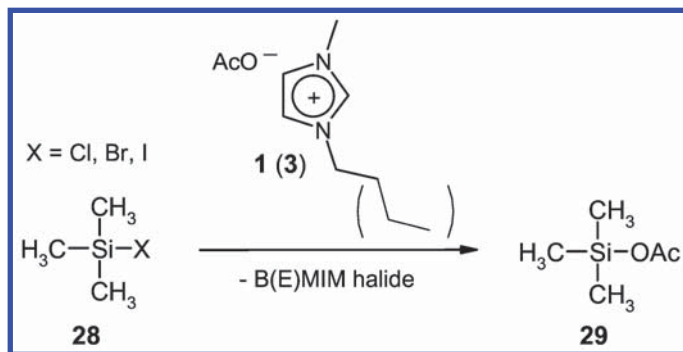
The last example for side reactions of IL anions to be given here is the attempted trimethylsilylation in 1-alkyl-3-methylimidazolium acetates (**1**, **3**) by common trimethylsilylating agents Me_3Si-X (TMS-X, **28**), such as TMS halides, hexamethyldisilazane, or *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA). Instead of silylating cellulose, the silylating agent converts the acetate anion into trimethylsilyl acetate (**29**), even nearly quantitatively (Scheme 8 and Figure 5). In the corresponding IL chlorides (**2**, **4**), by contrast, the trimethylsilylation proceeds as expected.

Conclusions

The heterocyclic IL cation reacts at C-2 with the reducing ends of cellulose and aldopyranose model compounds. The resulting modification of the cellulose might be rather minor relative to the number of glucopyranose units per cellulose chain, but might be of crucial importance for the processing of cellulosics and cellulose derivatives for use in medical and biological applications where even minor impurities might induce adverse effects. Furthermore, this means that the ionic liquid cannot be quantitatively recycled, which might affect process costs negatively. The use of 1-alkyl-3-methylimidazolium ILs in the processing of oxidized cellulosics, such as TEMPO-oxidized or periodate-oxidized cellulose, seems to be rather problematic, as the side reactions with the solvents will become predominant in those cases. By applying 2-alkylsubstituted ILs (*17*), the reaction with the reducing end of celluloses can be completely avoided, since the reacting center in the imidazolium cation is blocked by the substituent. The side reaction can at least be suppressed by the absence of bases and short reaction or contact times of less than 2 h, if practicable for the respective reaction system. Such bases can be auxiliary bases, or also common impurities in 1-alkyl-3-methylimidazolium-type ILs (imidazole, *N*-methylimidazole and *N*-alkylimidazole) as formed by thermal stress to the ILs.

With regard to non-inert anions, the use of BMIM acetate cannot be recommended in (organic and inorganic) esterifications of cellulose with acid
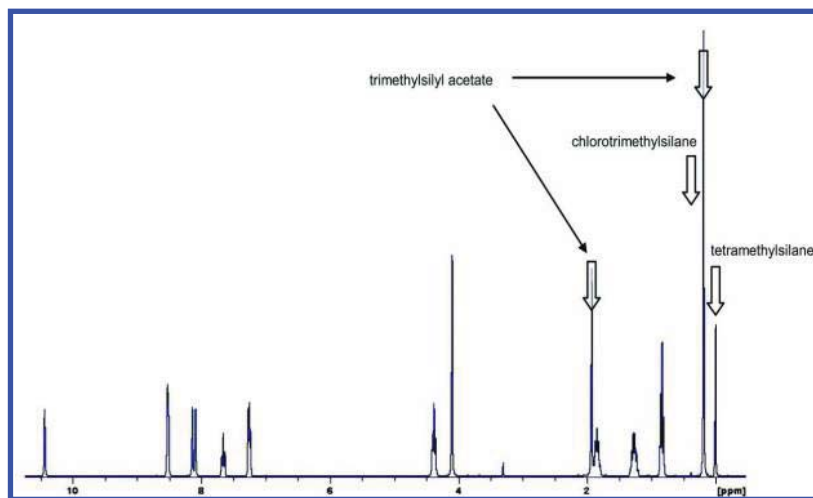
*Figure 5. ¹H NMR spectrum (ppm scale) of a mixture of BMIM-OAc (1),
Me₃Si-Cl and pyridine (molar ratio 2:1:1), acquired 15 min after mixing. While
the starting material Me₃Si-Cl has been almost completely consumed, the product
peak of trimethylsilyl acetate (29) becomes prominent. The resonances of the
acetate moieties in 1 and 29 coincide.*

chlorides and anhydrides, as the anion is converted into strongly acetylating species affording (partially) acetylated cellulose rather than the desired organic or inorganic esters. Cellulose methylation in B(E)MIM chloride and B(E)MIM acetate does not proceed, since the anion consumes the commonly used methylating agents methyl iodide and dimethyl sulfate by conversion into methyl chloride and methyl acetate, respectively, which exhibits largely inferior or no methylation behavior. Analogously, B(E)MIM acetate can also not be used for trimethylsilylations, since trimethylsilyl acetate is formed.

In conclusion, it was shown that 1-alkyl-3-methylimidazolium ILs react either with cellulose itself or with derivatization agents in the system. Both the cation and the anion of the IL might be involved in those side reactions, demonstrating unambiguously that ILs are not at all inert solvents for cellulose. These results recommend caution when progressing with the use of ILs in cellulose processing, especially with regard to usage of the cellulosic products in biological and biomedical applications.

Acknowledgements

Sciences Vienna, and Dr. Lothar Brecker, Institute of Organic Chemistry at the University of Vienna, for recording the NMR spectra.

References

1. Zhu, S.; Wu, Y.; Chen, Q.; Yu, Z.; Wang, C.; Jin, S.; Dinga, Y.; Wuc, G. Dissolution of cellulose with ionic liquids and its application: A mini-review. *Green Chem.* **2006**, *8*, 325–327.
2. Swatloski, R. P.; Spear, S. K.; John, D.; Holbrey, J. D.; Rogers, R. D. Dissolution of cellulose with ionic liquids. *J. Am. Chem. Soc.* **2002**, *124*, 4974–4975.
3. Wu, J.; Zhang, J.; Zhang, H.; He, J.; Ren, Q.; Guo, M. Homogeneous acetylation of cellulose in a new ionic liquid. *Biomacromol.* **2004**, *5*, 266.
4. Barthel, S.; Heinze, T. Acylation and carbanilation of cellulose in ionic liquids. *Green Chem.* **2006**, *8*, 301.
5. Heinze, T.; Schwikal, K.; Barthel, S. Ionic liquids as reaction medium in cellulose functionalization. *Macromol. Biosci.* **2005**, *5*, 520.
6. Heinze, T.; Pfeifer, A.; Petzold, K. Functionalization pattern of *tert*-butyldimethylsilyl cellulose evaluated by NMR spectroscopy.. *BioResources* **2008**, *3* (1), 79–90.
7. Sun, N.; Swatloski, R. P.; Maxim, M. L.; Rahman, M.; Harland, A. G.; Haque, A.; Spear, S. K.; Daly, D. T.; Rogers, R. D. Magnetite-embedded cellulose fibers prepared from ionic liquid. *J. Mater. Chem.* **2008**, *18*, 283–290.
8. Hermanutz, F.; Meister, F.; Uerdingen, E. New developments in the manufacture of cellulose fibers with ionic liquids. *Chem. Fiber Int.* **2006**, *6*, 342–343.
9. Liebert, T. Innovative concepts for the shaping and modification of cellulose.. *Macromol. Symp.* **2008**, *262*, 28–38.
10. (a) Röhrling, J.; Potthast, A.; Rosenau, T.; Lange, T.; Ebner, G.; Sixta, H.; Kosma, P. A novel method for the determination of carbonyl groups in cellulosics by fluorescence labeling. 2. Validation and applications. *Biomacromol.* **2002**, *3*, 969–975. (b) Potthast, A.; Röhrling, J.; Rosenau, T.; Borgards, A.; Sixta, H.; Kosma, P. A novel method for the determination of carbonyl groups in cellulosics by fluorescence labeling. 3. Monitoring oxidative processes. *Biomacromol.* **2003**, *4*, 743–749.
11. (a) Miyashita, A.; Kurachi, A.; Matsuoka, Y.; Tanabe, N.; Suzuki, Y.; Iwamoto, K.; Higashino, T. Synthesis and reactivities of 1,3-dimethyl-2-(α-hydroxybenzyl)imidazolium and 1,3-dimethyl-2-(α-hydroxybenzyl)benzimidazolium iodides. *Heterocycles* **1997**, *44*, 417–426. (b) Miyashita, A.; Matsuda, H.; Higashino, T. Catalytic action of azolium salts. III. Aroylation of *N*-phenylbenzimidoyl chlorides with aromatic aldehydes in the presence of 1,3-dimethylimidazolium iodide. *Chem. Pharm. Bull.* **1992**, *40*, (10), 2627–2631. (c) Davis, J. H., Jr.; Forrester, K. J. Thiazolium-ion based organic ionic liquids (OILs).

Novel OILs which promote the benzoin condensation. *Tetrahedron Lett.* **1999**, *40*, (9), 1621–1622. (d) Nair, V.; Bindu, S.; Sreekumar, V. *N*-Heterocyclic carbenes: Reagents, not just ligands. *Angew. Chem., Int. Ed.* **2004**, *43*, (39), 5130 –5135. (e) Estager, J.; Leveque, J.M.; Turgis, R.; Draye, M.Solventless and swift benzoin condensation catalyzed by 1-alkyl-3-methylimidazolium ionic liquids under microwave irradiation. *J. Mol. Catal. A: Chem.* **2006**, *256*, 261–264. (f) Tommasi, I.; Sorrentino, F.1,3-Dialkyl-imidazolium-2-carboxylates as versatile *N*-heterocyclic carbene-CO2 adducts employed in the synthesis of carboxylates and α-alkylidene cyclic carbonates. *Tetrahedron Lett.* **2009**, *50*, 104–107.

12. Aggarwal, V.K.; Emme, I.; Mereu, A. Unexpected side reactions of imidazolium-based ionic liquids in the base-catalyzed Baylis–Hillman reaction. *Chem. Commun.* **2002**, 1612–1613.

13. Köhler, S.; Liebert, T.; Schöbitz, M.; Schaller, J.; Meister, F.; Günther, W.; Heinze, T. Interactions of Ionic Liquids with Polysaccharides. 1. Unexpected acetylation of cellulose with 1-ethyl-3-methylimidazolium acetate. *Macromol. Rapid Commum.* **2007**, *28*, 2311–2317.

14. Yoneda, Y.; Ebner, G.; ; ; Takano, T.; Nakatsubo, F.PotthastA.RosenauT. Synthesis of the perdeuterated cellulose solvents 1-ethyl-3-methylimidazolium acetate (EMIM-OAc-d_{14}) and 1-butyl-3-methylimidazolium acetate (BMIM-OAc-d_{18}) and of 2-^{13}C-butyl-3-methylimidazolium acetate.. *J. Labeled Comp. Radiopharm.* **2009**, *52*, 223–226.

15. Adelwöhrer, C.; Takano, T.; Nakatsubo, F.; Rosenau, T. Chemical synthesis of ^{13}C-perlabeled cellulose with >99% isotopic enrichment according to a cationic ring-opening polymerization approach. *Biomacromol.* **2009**, in press.

16. Liebner, F.; Yoneda, Y.; Potthast, A.; Rosenau, T. Thermal degradation products of 1-alkyl-3-methylimidazolium ionic liquids and their side reactions in ionic liquid/cellulose solutions. *Holzforschung* **2009**, in press.

17. The protective effect of an alkyl-substitution at C-2 against side reactions of the IL has also be reported for Baylis–Hillman reaction in [bdmim][PF6] ionic liquid: Hsu, J. C.; Yen, Y. H.; Chu, Y. H. Baylis–Hillman reaction in [bdmim][PF6] ionic liquid. *Tetrahedron Lett.* **2004**, *45*, 4673–4676.

Ionic liquids as media for biomass processing: opportunities and restrictions

11th EWLP, Hamburg, Germany, August 16–19, 2010

Michael Schrems[1], Agnieszka Brandt[2,3], Tom Welton[2], Falk Liebner[1], Thomas Rosenau[1] and Antje Potthast[1,*]

[1] Christian-Doppler-Laboratory ''Advanced Cellulose Chemistry and Analytics'', Department of Chemistry, University of Natural Resources and Life Sciences, Muthgasse 18, A-1190 Vienna, Austria

[2] Department of Chemistry, Imperial College London, London, SW7 2AZ, UK

[3] The Porter Alliance, Imperial College London, London, SW7 2AZ, UK

*Corresponding author.
E-mail: antje.potthast@boku.ac.at

Abstract

The present study provides insight into the dissolution behavior of renewable materials in ionic liquids. Beech, spruce and rye straw were dissolved in 1-ethyl-3-methylimidazolium acetate as the ionic liquid of choice, which is currently one of the most frequently used cation-anion combinations among ionic liquids for biomaterial processing. The dissolution was followed by selective precipitation of cellulose, hemicelluloses, and lignin. The obtained lignin was analyzed with Curie-point pyrolysis gas chromatography/mass spectrometry (Cu-Py-GC/MS) and the separated cellulose/hemicellulose fractions with gel permeation chromatography (GPC). Time dependence of the dissolution process was studied on rye straw, eucalyptus kraft pulp and beech sulfite pulp. The results show a changing dissolution profile over time, which is due to progressing degradation of the cellulose in the ionic liquid.

Keywords: cellulose; cellulose degradation; Curie-point pyrolysis gas chromatography/mass spectrometry (Cu-Py-GC/MS); fractionation; ionic liquids (ILs); lignin; molecular weight distribution (MWD); renewable materials; size-exclusion chromatography (SEC).

Introduction

Cellulose is the most abundant natural organic polymer on earth (Klemm et al. 2005). Due to fading petrochemical (non-renewable) resources, the interest on biodegradable and renewable organic raw materials is steadily increasing. While cellulose production has been well established for centuries, the use of other constituents of plant cell walls, such as hemicelluloses and lignin still has limitations. In particular, this is observed with large scale biorefinery applications in focus

or when non-woody resources, such as agricultural waste products are the raw materials (Busch et al. 2006). At the molecular level, one of the main reasons for such problems are the intermolecular bonds between the entangled large macromolecular components with low solubility, which need different solvents and the resulting difficulties in their dissolution and clean fractionation (Klemm et al. 2005).

An important issue in biorefinery research is the development of suitable analytics. Many conventional analytical approaches fail in this context because they are suited for characterization of pure products or simple reaction mixtures, but not for such overly complex multicomponent mixtures as encountered in biomass processing (biorefineries). Furthermore, robust techniques are required, which in the best case could also be applied online or quasi online. Strongly interacting solvents are needed to achieve complete dissolution of the components. Even for purified celluloses, only a very limited number of solvent systems such as N,N-dimethylacetamide/lithium chloride (DMAc/LiCl) or 1,3-dimethyl-2-imidazolidinone/lithium chloride (DMI/LiCl) are currently available for dissolution in a transparent, molecular disperse form. Not all celluloses are soluble this way and the presence of hemicelluloses and in particular lignin diminishes further solubility. In most cases, chemical or mechanical pretreatments are needed before complete dissolution of woody biomass.

Ionic liquids (ILs) have a high potential as powerful cellulose solvents (Xie et al. 2007; Cao et al. 2009). According to the literature, this potential is particularly connected to ionic liquids containing ammonium, pyridinium or imidazolium cations, hence nitrogen-based cations (Honglu and Tiejun 2006; Zhu et al. 2006; El Seoud et al. 2007; Jia et al. 2010; Liebert 2010; Liebner et al. 2010; Nakamura et al. 2010a,b). Phosphonium and sulfonium-based ionic liquid cations do not behave similarly well in this regard. In addition, an asymmetric anion is required to form melts with cellulose. Out of the nitrogen-based ionic liquid cations currently available, imidazolium appears to be the most suitable one for cellulose processing, pyridinium ionic liquids tend to degradation if no protective gas is applied (Barthel and Heinze 2006). Furthermore, selected ionic liquids have the ability to dissolve other main constituents of lignocellulosic feedstocks, such as lignin, in their genuine form without any prior derivatization and at considerably high concentration (Pu et al. 2007). Remarkably, this dissolution ability is not only effective for the isolated components but also for the natural mixtures or composites. This applies even to non-modified wood (Kilpelainen et al. 2007). Dissolving cellulose together with the whole surrounding matrix gives a unique opportunity to analyze the major plant cell wall components in their pristine state and it might give major impetus

to biorefinery analytics. The expectation is that if suitable anti-solvents are found, a fractionation of wood components into lignin and different polymeric carbohydrates should be feasible, which thus could be separated in a rather unaltered form (Fort et al. 2007). Despite these opportunities, several restrictions are connected to the use of ionic liquids as biomass solvents. Size and density of the wooden material have a considerable effect on the pretreatment efficiency, which can be explained by the accessible surface area. Sufficient recycling and purification of the processed ionic liquid is still not available and remains as one of the most challenging obstacles before industrial process feasibility can be achieved (Li et al. 2010).

The first part of this study addresses such a fractionation process by comparing different precipitation baths and procedures, with a strong emphasis on analytical aspects. The carbohydrate-based material will be analyzed by gel permeation chromatography (GPC) and the obtained insoluble lignin fractions by means of Curie-point pyrolysis/gas chromatography/mass spectrometry (Cu-Py-GC/MS). The second part of this study addresses the dissolution of lignocellulosic materials in the solvent 1-ethyl-3-methylimidazolium acetate (EmimOAc). Samples taken at suitable intervals during the dissolution process and the resulting time dependent profiles of molecular weight distribution (MWD) will be discussed.

Materials and methods

Chemicals

Chemicals were obtained from commercial sources and were of the highest purity available. N,N-Dimethylacetamide (DMAc) was obtained from Promochem Chemicals, Germany. Beech and spruce powder (milled to <32 μm) was obtained from Josef Rettenmaier & Söhne GmbH and Co. KG, Rosenberg, Germany. The unbleached eucalyptus kraft pulp (EKP) was obtained from Lenzing AG, Lenzing, Austria and had a kappa number of 25. Ozone bleached beech sulfite pulp (BBSP) was obtained from Lenzing AG, Lenzing, Austria. Rye straw obtained from different local suppliers in Lower Austria was milled to <1 mm. The ionic liquid EmimOAc was purchased from Sigma Aldrich in BASF quality (≥95%) and used without further purification. 1-Butyl-3-methylimidazolium acetate (BmimOAc) was synthesized using 1-butyl-3-methylimidazolium bromide (Wells et al. 2008) and silver acetate, and subsequently purified to highest achievable purity.

Fractionating procedure

Five hundred milligram of material (beech, spruce, rye straw and pulp) was dissolved in 10 ml of EmimOAc and stirred at 110°C until complete dissolution occurred as described by Sun et al. (2009). Aliquots of the solution were taken and treated in the different precipitation baths consisting of a 1:1 mixture of water and acetone (Sun et al. 2009) or ethanol (Balensiefer et al. 2008a,b). The precipitated fraction containing mainly cellulose was washed with aliquots of the precipitation bath mixture, rinsed with ethanol and activated as described below. The ionic liquid containing filtrate was concentrated and treated with hot water to precipitate the containing lignin, which was subsequently filtered off and dried (70°C, 24 h).

GPC System

For GPC measurements, the set-up as described by Röhrling et al. (2002) was followed. Details: online degasser, Dionex DG-2410; Kontron 420 pump; pulse damper; autosampler, HP series 1090; column oven, Gynkotek STH 585; multi-angle laser light scattering (MALLS) detector; refractive index (RI) detector, Shodex RI-101. DMAc/LiCl (0.9% w/v), filtered through a 0.02 μm filter was the eluent. The sample was injected automatically, chromatographed on four serial GPC columns and monitored by fluorescence, MALLS (Wyatt Heleos 658 nm or Wyatt Dawn DSP 488 nm) and RI detection. Parameters of GPC: flow, 1.00 ml min^{-1}; four columns, PL gel mixed A LS, 20 μm, 7.5×300 mm; detectors, MALLS-RI; injection volume, 100 μl; run time, 45 min. Data evaluation: standard Chromeleon and Astra software.

Activation and dissolution of pulp samples

To achieve a molecular disperse solution in DMAc/LiCl (9% w/v), the pulp samples had to be activated by solvent exchange (H$_2$O to DMAc) followed by agitating in DMAc and filtration, which produced efficiently activated, i.e., readily soluble samples (Röhrling et al. 2002).

Cu-Py-GC/MS was performed with a CPP-40 pyrolyzer (GSG Mess- und Analysegeräte GmbH, Bruchsal, Germany) coupled with a GC 6890 and MSD 5973 (Agilent Technologies). The sample (260 μg) was pyrolysed at 600°C (Fecralloy™) for 10 s. The pyrolysate was carried by Helium into the inlet (250°C, split 1:20) of the gas chromatograph. Separation was achieved on a fused silica HP-5 ms column (30 m, 0.25 mm, 25 μm) and a column flow of 1.0 ml min^{-1}. Oven program: 50°C (5 min), 5°C min^{-1} to 180°C, then 10°C min^{-1} to 280°C (9 min). Auxiliary temperature: 250°C (18 min), 10°C min^{-1} to 280°C (14 min). Mass spectrometer: EI mode (70 eV); ion source 230°C; quadrupole 150°C, 7.6×10^{-6} Torr. Peak assignment was accomplished based on the NIST 2005 mass spectra database.

Results and discussion

Dissolution, fractionation and analysis of biomass components

Ionic liquids have the power to dissolve renewable materials in a largely unaltered form.

Although there is a reaction between imidazolium type cations and the reducing end of celluloses, particularly in aged ionic liquids, this modification is minor (Ebner et al. 2008; Schrems et al. 2010). However, it is promising that cellulose, hemicelluloses and lignin can be separated by applying suitable anti-solvents (see Figure 1). In this study, two different separation procedures were compared regarding performance and purity of the obtained fractions.

In the first separation procedure, a 1:1 mixture of acetone and water was applied as described by Sun et al. (2009). The second separation procedure follows patents of BASF (Balensiefer et al. 2008a,b) based on a 1:1 mixture of ethanol and acetone at 40°C. No significant differences between the two methods regarding the MWD were observed (Figure 2a). The different heights of the peaks are due to different concentrations of the samples.
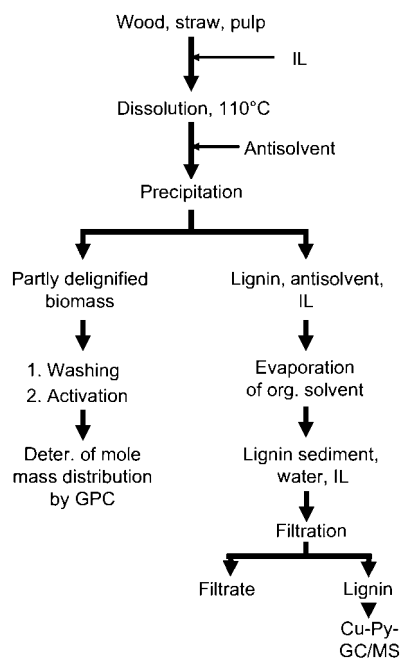
Figure 1 Flow chart showing biomass processing and executed analyses.

After separation of the fraction rich in cellulose according to precipitation method number one (acetone and water 1:1, 12.5 ml), the GPC elution profiles (Figure 2b) showed the main cellulose peak with a well separated hemicellulose peak centered at approximately 23 min retention time for beech and rye straw, whereas in the case of spruce just a shoulder was visible. These GPC distributions profiles are typical for mixtures of hemicellulose-containing celluloses, having a distinct hemicellulose peak at significantly lower MW. This obvious difference in the separation of hemicelluloses can be explained by the different constitution of the hemicelluloses. Xylan, which is typical for hardwood and straw (Jones 1978) is clearly separated from the cellulose peak. The predominant glucomannan in softwood (Moreira and Filho 2008) has a higher similarity to cellulose and is therefore appearing closer to the bulk cellulose peak. This correlates well with MW profiles of softwood pulps for both, kraft and sulfite pulping, which did not show a well separated hemicellulose peak in GPC. In contrast, for hardwood samples, the xylan peak was much better separated (Henniges et al. 2011).

Following the separation of the polysaccharides, the IL-containing filtrate was evacuated to remove the organic solvents (acetone and ethanol). Precipitation of lignin was accomplished by diluting the remaining aqueous IL phases, which significantly reduced the solubility of lignin. The obtained lignin was filtered off, dried (70°C, 24 h) and analyzed with analytical Cu-Py-GC/MS with regard to lignin purity and chemical integrity in terms of preserving the native ratio of 4-hydroxyphenyl-, 3-methoxy-4-hydroxyphenyl-, and 3,5-dimethoxy-4-hydroxyphenyl units. Pyrolytic lignin contents were calculated from the cumulated peak areas of 53 pyrolysis products originating from thermal lig-
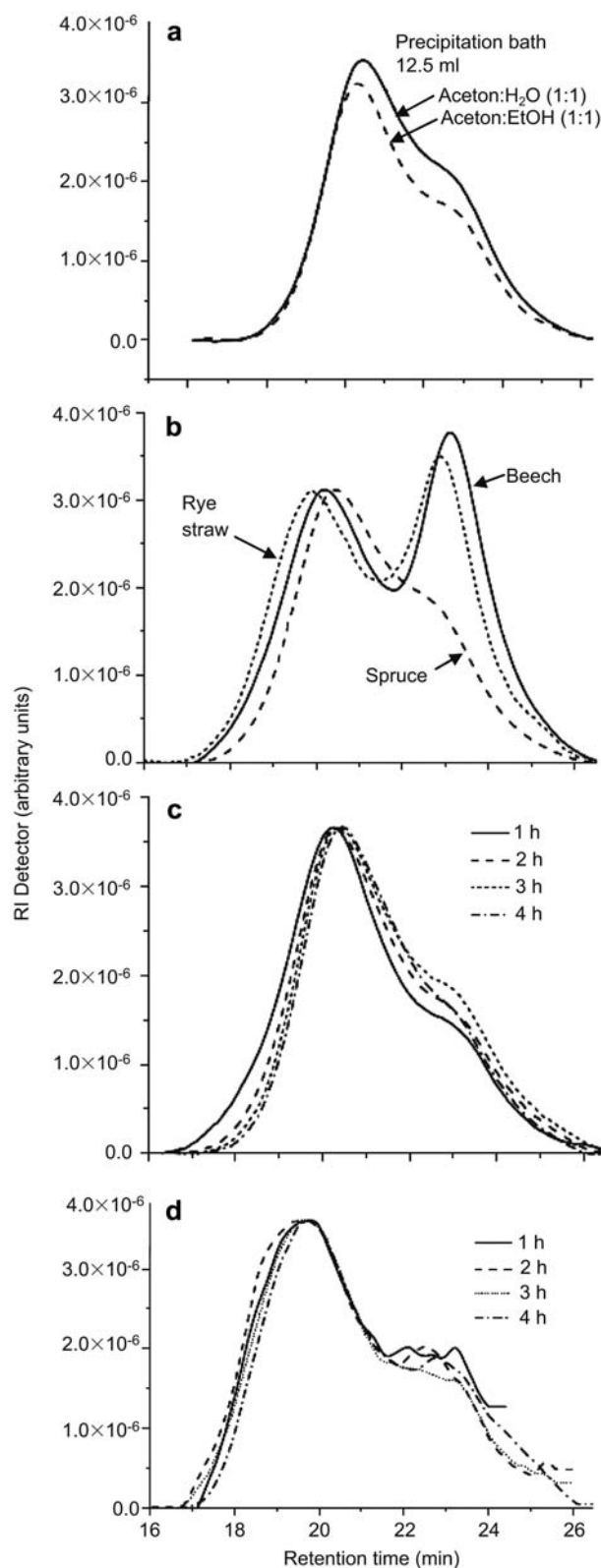

Figure 2 GPC elution profiles (0.9% DMAc/LiCl).
(a) Comparison between different cellulose precipitation procedures from ILs. (b) Beech, spruce and rye straw carbohydrate fractions obtained by one bath (number one). (c) Unbleached eucalyptus kraft pulp profile over time. (d) Rye straw profile over time.
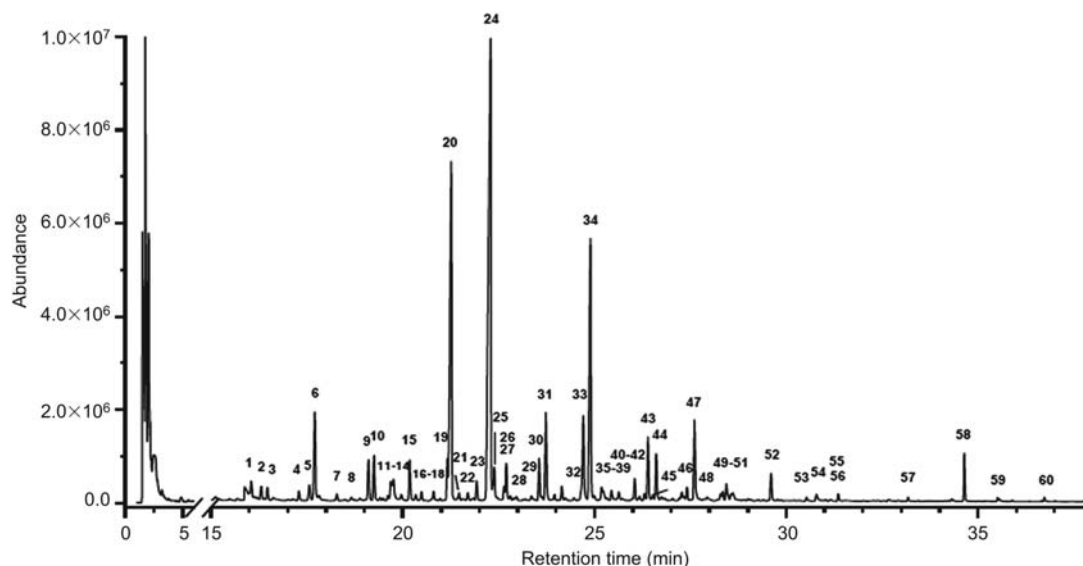
Figure 3 Curie-point pyrogram of beech lignin precipitated from EmimOAc with water.

nin degradation and the total peak area corrected by the integrals of IL-derived peaks and the ''gas'' peak (Figure 3 and Table 1 for the pyrogram of beech lignin precipitated with acetone and water including peak assignment). The results confirm that comparatively pure lignins with pyrolytical lignin contents of 96–99% can be obtained by hot water precipitation from respective solutions of wood samples in mixtures of EmimOAc, acetone, water or EmimOAc, acetone, ethanol. In addition, the results demonstrate comparable lignin purity for both of the tested fractionating procedures. The nearly constant ratio of H-, G- and S-type pyrolysis products [i.e., 4-hydroxyphenyl- (H units), 3-methoxy-4-hydroxyphenyl- (G units), and 3,5-dimethoxy-4-hydoxyphenyl-based (S units)] of the bulk beech wood (0.8, 56.5 and 42.7, respectively) and of the lignin isolated from the sample (0.8, 51.3 and 47.9, respectively) by precipitation with acetone and water furthermore demonstrated a good preservation of its molecular structure.

Dissolution and precipitation profile of renewable materials in ILs

The dissolution process can be better understood by observing the course of dissolution over time. In this context both dissolution and precipitation profiles have been established. There are two borderline cases conceivable: (1) the biomaterial dissolves gradually and during this time the composition of the dissolved fraction remains constant over time and thus no component is preferentially dissolved and (2) a constant change takes place from a starting composition of dissolved material to its final concentration, implying a different solubility of the components and a certain discrimination effect.

Following the precipitation behavior of woody or non-woody biomaterials in ionic liquids is difficult because normally large amounts of dissolved material tend to precipitate even when small amounts of anti-solvent are applied. In our

case, 500 mg of lignocellulosic material have been dissolved in 10 ml of EmimOAc. After a complete dissolution, small volumes of a 1:1 mixture of acetone and water were added to the IL solution. The material precipitated was separated at each step by centrifugation and the supernatant was transferred back.

Despite the precipitation behavior, analysis of the dissolution behavior is much easier. The same solvent or solute ratios were used and aliquot samples were taken every hour. Fresh EmimOAc was added each time after a sample was taken to guarantee identical conditions and sampling volumes for the subsequent samplings. The obtained samples were treated and ''activated'' for GPC studies in the same manner as described above. The dissolution profile of unbleached eucalyptus kraft pulp in EmimOAc over a 4 h period is shown (Figure 2c). Evidently, the MW of the dissolved molecules was decreasing significantly over time: the material dissolved first had a higher MW than the material dissolved in later stages. The MW dropped down from 3.1×10^5 g mol^{-1} to 2.5×10^5 g mol^{-1} in just 4 h. This allows for two conclusions, that is, either high MW cellulose fractions are preferentially dissolved or this effect is caused by a progressing degradation of the already dissolved material under dissolution conditions. A similar experiment for rye straw was conducted (Figure 2d). Comparable results were observed although the effect was not as distinct as for the eucalyptus pulp.

Clarification of the reasons for the MWD shift

To clarify which of the two possible processes are responsible for the surprising change in molar weight with ongoing dissolution in the IL, time-dependent studies of the MWD after complete dissolution of the pulp were completed. In the case of preferential dissolution, no MW shift should be observed once the complete material was dissolved. In the opposite case (degradation occurs), MWD shift should be

Table 1 Analytical Curie-point pyrolysis of beech lignin precipitated from EmimOAc by water addition: retention times and peak assignment.

Number	Retention (min)	Assignment	Number	Retention (min)	Assignment
1	16.05	Pentanedioic acid 2ME	31	23.73	Z-Isoeugenol
2	16.31	1,2-Dimethoxyphenol	32	24.73	4-Methylsyringol
3	16.47	2-Ethoxyphenol	33	24.65	3,4,5-Trimethoxybenzaldehyde
4	17.29	2-Methylguaiacol	34	24.89	E-Isoeugenol
5	17.56	3-Methylguaiacol	35	25.01	4-Allylveratrol
6	17.70	4-Methylguaiacol	36	25.18	4-Acetylveratrol
7	18.29	Pentanedioic acid EME	37	25.24	Guaiacol derivative
8	18.66	4-Vinylphenol	38	25.43	4-Acetylsyringol
9	19.11	4-Methylveratrol	39	25.64	Veratrylaldehyde
10	19.26	Syringol	40	26.05	E-4-(Prop-1-en-1-yl)veratrol
11	19.41	2-Ethoxy-4-methylphenol	41	26.17	4-Allylsyringol
12	19.49	2-Ethoxy-5-methylphenol	42	26.30	2,4,6-Trimethoxybenzaldehyde
13	19.79	3-Methoxy-1,2-benzenediol	43	26.40	5-Vinyl-1,2,3-trimethoxybenzene
14	19.96	3-Methylveratrol	44	26.52	Guaiacol derivative
15	20.19	4-Ethylguaiacol	45	26.64	4-Ethylsyringol
16	20.33	3-Ethylguaiacol	46	27.28	5-Allyl-1,2,3-trimethoxybenzene
17	20.49	4-Methylguaiacol EE	47	27.61	Guaiacylacetone
18	20.82	5-Methylguaiacol EE	48	27.95	Veratrylacetone
19	21.15	1,2,3-Trimethoxybenzene	49	28.29	Veratric acid ME
20	21.29	4-Vinylguaiacol	50	28.34	Z-5-(Prop-1-en-1-yl)-1,2,3-trimethoxybenzene
21	21.47	4-Ethylguaiacol ME	51	28.63	5-Ethyl-1,2,3-trimethoxybenzene
22	21.69	5-Vinylguaiacol	52	29.61	E-5-(Prop-1-en-1-yl)-1,2,3-trimethoxybenzene
23	21.94	1,2,3-Trimethoxybenzene	53	30.54	4-(Prop-1-en-1-yl)syringol EE
24	22.26	Syringol	54	30.80	4-(Prop-1-en-1-yl)syringol
25	22.38	Eugenol	55	31.14	Syringic acid 2ME
26	22.64	4-Propylguaiacol	56	31.36	Tetradecanoic acid ME
27	22.70	4-Vinylveratrol	57	33.18	Pentadecanoic acid ME
28	22.99	4-Hydroxybenzoic acid 2ME	58	34.65	Hexadecanoic acid ME
29	23.37	Syringol EE	59	35.52	Hexadecanoic acid EE
30	23.57	5-Me-1,2,3-trimethoxybenzene	60	36.74	Octadecanoic acid ME

2ME, dimethylester; EME, ethylmethylester; EE, ethylether; ME, methylether.

observable for the completely dissolved material. Tests with unbleached eucalyptus kraft pulp doubtlessly revealed that the second case is true, i.e., a progressive degradation of the already dissolved material occurs. At this stage, however, it was not clear if the degradation was due to side reactions of the solvent itself or if it was caused by impurities in commercially available ILs. Therefore, the same experiment was repeated with a neat, authentic sample of IL (BmimOAc). The initially observed trend also occurred in the pure reference solvent, and surprisingly, the effect was even more pronounced than in the commercially available one (Figure 4a). Accordingly, high purity ILs have a higher degradation reactivity, that is, the effect is inherent to the IL.

Identical experiments have been conducted with a BBSP. The increased degradation efficiency of pure IL was confirmed (Figure 4b). Furthermore, a strong temperature dependency of the degradation was demonstrated. Tests at 85°C revealed a significantly slower degradation than at higher temperatures. A comparison between measured MWs after 24 h as a function of the solution temperature was examined (Figure 4c). In contrast, processing at 110°C causes severe degradation; this effect is considerably reduced at

85°C and almost non-existent at 60°C. Similar findings on the temperature-dependent severeness of cellulose degradation have been published for the system DMAc/LiCl (Potthast et al. 2002). Our results provide evidence that there is a significant loss in the molecular weight over time upon dissolution of lignocellulosic matter in IL, which is not due to a discrimination effect during dissolution but instead as a result of cellulose degradation advancing over time caused by side reactions with the imidazolium-based IL.

GPC sample activation cannot be avoided

Solvent exchange experiments have been conducted to check the possibility of avoiding the time-consuming activation process mentioned for GPC analysis by means of IL as solvent, which is time consuming. Different lignocellulosic materials were dissolved in EmimOAc and were then transferred into solutions of *N,N*-dimethylacetamide containing 0.9% and 9% LiCl, respectively. Unfortunately, the dissolved material precipitated and could not be re-dissolved again. Thus, the ''activation steps'' for GPC analysis are inevitable so far.
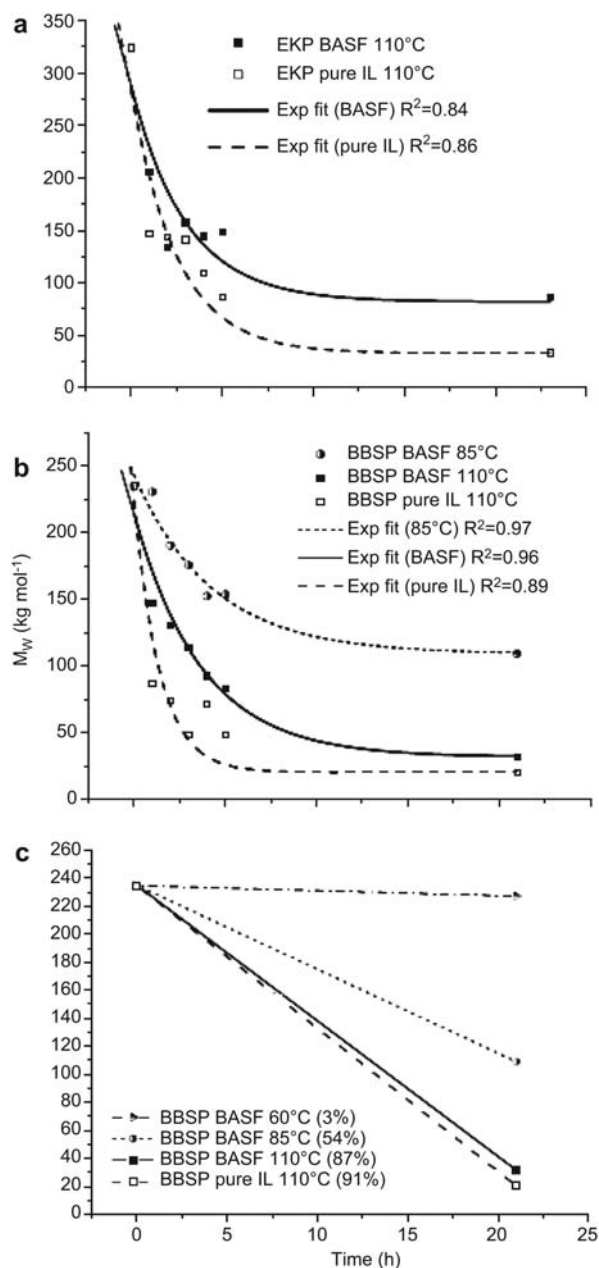
Figure 4 MW behavior after complete dissolution.
(a) Degradation of EKP in ILs after complete dissolution. (b) Degradation of BBSP in ILs after complete dissolution indicating a strong temperature dependency. (c) Temperature-dependent cellulose degradation in ILs in percentage of original MW.

Conclusions

This study confirms that ionic liquids have the ability to dissolve lignocellulosic materials (wood, straw) and that fractionation of the constituents can be effectuated when the right anti-solvents are applied for precipitation. The precipitated pure lignins were shown to keep their chemical composition, as the native ratios of H/G/S units remain unaltered.

Unexpectedly, the MWDs of the cellulose-rich fraction are not constant in the course of time-dependent dissolution

experiments. The changing MW was shown to be a result of progressing degradation of the cellulose in ionic liquid. This effect is more pronounced in pure IL and at higher temperatures. This observation has consequences in terms of alternative green strategies for biomass processing by means of ionic liquids. The development of biorefinery processes needs the support of adequate analytical methodology.

References

Balensiefer, T., Brodersen, J., D'Andola, G., Massonne, K., Freyer, S., Stegmann, V. (2008a) Method for producing glucose by enzymatic hydrolysis of cellulose that can be pretreated with an ionic liquid containing a polyatomic anion. PCT Int. Appl. WO 2008/090155 A1.

Balensiefer, T. (2008b) Method for producing glucose by enzymatic hydrolysis of cellulose that is obtained from material containing lingo-cellulose using ionic liquid that comprises a polyatomic anion. PCT Int. Appl. WO 2008/090156 A1.

Barthel, S., Heinze, T. (2006) Acylation and carbanilation of cellulose in ionic liquids. Green Chem. 8:301–306.

Busch, R., Hirth, T., Liese, A., Nordhoff, S., Puls, J., Pulz, O., Sell, D., Syldatk, C., Ulber, R. (2006). The utilization of renewable resources in German industrial production. Biotechnol. J. 1:770–776.

Cao, Y., Wu, J., Li, H., Zhang, Y., He, J. (2009) Room temperature ionic liquids (RTILs): a new and versatile platform for cellulose processing and derivatization. Chem. Eng. J. 147:13–21.

Ebner, G., Schiehser, S., Potthast, A., Rosenau, T. (2008) Side reaction of cellulose with common 1-alkyl-3-methylimidazolium-based ionic liquids. Tet. Lett. 49:7322–7324.

El Seoud, O.A., Koschella, A., Fidale, L.C., Dorn, S., Heinze, T. (2007) Applications of ionic liquids in carbohydrate chemistry: a window of opportunities. Biomacromolecules 8:2629.

Fort, D.A., Remsing, R.C., Swatloski, R.P., Moyna, P., Moyna, G., Rogers, R.D. (2007) Can ionic liquids dissolve wood? Processing and analysis of lignocellulosic materials with 1-n-butyl-3-methylimidazolium chloride. Green Chem. 9:63–69.

Henniges, U., Kostic, M., Borgards, A., Rosenau, T., Potthast, A. (2011) Dissolution behavior of different celluloses. Biomacromolecules 12:871–879.

Honglu, X., Tiejun, S. (2006) Wood liquefaction by ionic liquids. Holzforschung 60:509–512.

Jia, S., Cox, B.J., Guo, X., Zhang, Z.C., Ekerdt, J.G. (2010) Decomposition of a phenolic lignin model compound over organic N-bases in an ionic liquid. Holzforschung 64:577–580.

Jones, J.K.N. (1978). Hemicelluloses in hardwoods growing on southern pine sites. Wood and Fiber 9:295–307.

Kilpelainen, I., Xie, H., King, A., Granstrom, M., Heikkinen, S., Argyropoulos, D. (2007) Dissolution of wood in ionic liquids. J. Agric. Food Chem. 55:9142–9148.

Klemm, D., Heublein, B., Fink, H.P., Bohn, A. (2005) Cellulose: fascinating biopolymer and sustainable raw material. Angew. Chem. Int. Ed. 44:3358–3393.

Li, B., Asikkala, J., Filpponen, I., Argyropoulos, D.S. (2010) Factors affecting wood dissolution and regeneration of ionic liquids. Ind. Eng. Chem. Res. 49:2477–2484.

Liebert, T. (2010) Cellulose solvents – remarkable history, bright future. In: Cellulose Solvents: For Analysis, Shaping and Chemical Modification. Eds. Liebert et al. ACS Symposium Series, American Chemical Society, Washington DC.

Liebner, F., Patel, I., Ebner, G., Becker, E., Horix, M., Potthast, A., Rosenau, T. (2010) Thermal aging of 1-alkyl-3-methylimidazolium ionic liquids and its effect on dissolved cellulose. Holzforschung 64:161–166.

Moreira, L.R.S., Filho, E.X.F. (2008). An overview of mannan structure and mannan-degrading enzyme systems. Appl. Microbiol. and Biotechnol. 79:165–178.

Nakamura, A., Miyafuji, H., Saka, S. (2010a) Liquefaction behavior of Western red cedar and Japanese beech in the ionic liquid 1-ethyl-3-methylimidazolium chloride. Holzforschung 64:289–294.

Nakamura, A., Miyafuji, H., Saka, S., Mori, M., Takahashi, H. (2010b) Recovery of cellulose and xylan liquefied in ionic liquids by precipitation in anti-solvents. Holzforschung 64:77–79.

Potthast, A., Rosenau, T., Sixta, H., Kosma, P. (2002) Degradation of cellulosic materials by heating in DMAc/LiCl. Tet. Lett. 43: 7757–7759.

Pu, Y., Jiang, N., Ragauskas, A.J. (2007) Ionic liquid as a Green solvent for lignin. J. Wood Chem. Technol. 27:23–33.

Röhrling, J., Potthast, A., Rosenau, T., Lange, T., Ebner, G., Sixta, H., Kosma, P. (2002) A novel method for the determination of carbonyl groups incellulosics' by fluorescence labeling. 1. Method development. Biomacromolecules 3:959–968.

Schrems, M., Ebner, G., Liebner, F., Becker, E., Potthast, A., Rosenau, T. (2010) Side reactions in the system cellulose/1-alkyl-3-methyl-imidazolium ionic liquid. In: Cellulose Solvents: For Analysis, Shaping and Chemical Modifications. Eds. Liebert, T., Heinze, T., Edgars, K. ACS Symposium Series, American Chemical Society, Washington, DC.

Sun, N., Rahman, M., Qin, Y., Maxim, M.L., Rodriguez, H., Rogers, R.D. (2009) Complete dissolution and partial delignification of wood in the ionic liquid 1-ethyl-3-methylimidazolium acetate. Green Chem. 11:646–655.

Wells, T.P., Hallett, J.P., Williams, C.K., Welton, T. (2008) Esterification in ionic liquids: the influence of solvent basicity. J. Org. Chem. 73:5585–5588.

Xie, H., King, A., Kilpelainen, I., Granstrom, M., Argyropoulos, D. (2007) Thorough chemical modification of wood-based lignocellulosic materials in ionic liquids. Biomacromolecules 8: 3740–3748.

Zhu, S., Wu, Y., Chen, Q., Yu, Z., Wang, C., Jin, S., Dinga, Y., Wu, G. (2006) Dissolution of cellulose with ionic liquids and its application: a mini-review. Green Chem. 8:325–327.

Understanding the impact of super critical carbon dioxide on the delignification mechanism during Organosolv pulping - a model compound study.

Michael Schrems, Falk Liebner, Markus Betz, Martin Zeilinger,

Thomas Rosenau and Antje Potthast*

Christian-Doppler-Laboratory "Advanced Cellulose Chemistry and Analytics", Department of Chemistry, University of Natural Resources and Life Sciences Vienna, Austria

*Corresponding author: Antje Potthast, antje.potthast@boku.ac.at**; Fax: +43-1-47654-6059

Abstract: In this paper we investigated delignification pathways occurring during Organosolv pulping by means of monomeric and dimeric lignin model substances. This study clearly showed that there is a strong dependency of the degradation rate of all model compounds of the temperature. Model compounds carrying a "free" phenolic group were found to react via a quinone methide intermediate and to be significantly more reactive than their methoxylated counterparts, reacting via nucleophilic substitution due to their inability to form such intermediates. A radical reaction course could be ruled out due to low activation energies and unincisive oxidation of cellulose. Super critical carbon dioxide was found to enhance the delignification process by lowering the activation energy and accelerating the model substance decay wherefore its application in Organosolv concepts is proposed. The observed subsequent slow down in the formation of the end product is potentially caused by the formation of a stabilizing carbonate.

Keywords: Organosolv; delignification; model substance; kinetics; sc CO_2

INTRODUCTION

Valorization of re-growing sources and biomaterial research increasingly gain importance these days due to the slowly but surely dwindling global fossil resources.[1] The development of alternative technologies for biomass processing comprises all major industries in the energy, chemistry or material sectors.

Organosolv pulping – delignification of biomass with hot aqueous aliphatic alcohols – has been first described in 1931.[2] However, significant advances in this technology have been made only at the beginning of the 1990s in an attempt to establish an environmental benign alternative to the established alkaline (sulfate, soda) or sulfite (neutral, acidic) wood pulping processes which all however have the drawback to generate enormous amounts of inorganic or sulfurous by-products. While wood was in the focus as the main raw material especially in the beginning of Organosolv development, harvest residues from annual plants have been increasingly moved into the limelight of pulping activities these days. A better understanding of the pulping chemistry is an inevitable prerequisite to optimise the pulping process with regard to the required sources, pulp quality, and by-product management and to establish the Organosolv technology on an industrial scale.

Systematic investigations towards the complex reaction sequences occurring upon delignification under Organosolv conditions were conducted by McDonough.[3] He reported cleavage of ether linkages as key for lignin breakdown and the probability of α- and β-ether cleavage strongly affected by the prevalent pH. Cleavage of β-ethers was found to proceed under both acidic and alkaline conditions enhanced by the presence of nucleophilic additives in the latter case. On the contrary α-ethers are easily hydrolyzed under acidic conditions whereas under alkaline conditions α-ether bonds are only broken in units containing "free" phenolic groups. Even though methanol/water mixtures give similar yields, it is meanwhile accepted that the use of ethanol guarantees higher lignin purities with regard to residual carbohydrate con-

tents.[4] Kishimoto and Sano later studied the effects of high-boiling solvents (HBS) such as aqueous 1,3-butanediol instead of aqueous ethanol aiming to further advance the Organosolv technology. [5-10] Model compound experiments using the β-*O*-4-linked dimer guaicylglycerol-β-guaiacyl ether evidenced that lignin depolymerization, in particular the cleavage of β-*O*-4 bonds, follows a radical pathway. This was concluded from the formation of several dimers and oligomers under the studied conditions (70 wt% aq. 1,3-butanediol, 160–200°C).

Supercritical carbon dioxide (scCO$_2$) as a co-solvent is hypothesized to have beneficial effects on pulping as it generates an anomalous porosity and lamellar structure within the treated materials. This effect leads to an increased accessibility of the organic matter for the pulping reagents, e.g. the ethanol/water mixture and should hence improve the efficiency of the pulping process.[11,12]

The current paper communicates the results of advanced model compound study aiming at both, a better understanding of the delignification pathways occurring under Organosolv conditions and of the effect of supercritical carbon dioxide on the delignification efficiency. Two pairs of monomeric and dimeric guaiacyl-type model compounds were chosen. Each of them consists of one representative that carries a "free" phenolic group in para-position to the alkyl side chain. In the corresponding counterparts the phenolic group is replaced by a methoxy group that would prevent these compounds from the formation of quinone methides.

EXPERIMENTAL

Chemicals

2-Methoxy-4-acetylphenol (4-Acetylguaiacol), 1,2-dimethoxy-4-acetylbenzene (4-acetylveratrol), 2-methoxy-4-vinylphenol (4-vinylguaiacol) and sodiumborohydride were purchased from Sigma Aldrich (St. Louis, MO, USA) and used without further purification.

Model compound studies under "standard" Organosolv conditions (ethanol/water)

Experiments were performed in a 0.02 l micro reactor (Parr Instruments, 4590 Series). 20 mg of 2-Methoxy-4-(1-hydroxyethyl)phenol (1-guaiacyl-ethanol, Apocynol, compound **1a** in Scheme 1) and 1,2-Dimethoxy-4-(1-hydroxyethyl)benzene (1-veratryl-ethanol, **1b**) was placed in a glass insert of a stainless steel reactor and dissolved in 10 ml of 50% (v/v) aqueous ethanol. The reactor was sealed and heated to the desired temperature (140-190°C, steps of 10°C). At the end of the respective reaction time the reactor was immediately cooled down below 40°C, depressurised, and the yellowish to brownish solution was subjected to HPLC and GC/MS analysis, respectively.

Model compound studies under Organosolv conditions using CO_2 as a co-solvent

Experiments were performed in a 0.2 l autoclave with jacketed heater (SEPAREX, France) which was pre-heated to 80°C. 20 mg of the respective 1-guaiacylethanol (**1a**) and 1-veratrylethanol (**1b**), respectively, was placed in a small beaker and dissolved in 10 ml of a 1:1 mixture of ethanol and water. The beaker was then inserted into the reactor which was subsequently sealed. The reaction chamber was pressurised with CO_2 (6 MPa) to obtain a homogeneous CO_2-expanded ethanolic phase already below the particular reaction temperature. After flash-heating the reaction mixture to the desired temperature (140-180°C) the pressure was further increased to 16 MPa (t=0) using a hand-piston-pump (Sitec, Switzerland) and left under these conditions until the respective reaction time had elapsed. At the end of the respective reaction time the reactor was immediately cooled down below 40°C, depressurised, and the yellowish to brownish solution was subjected to HPLC analysis.

Synthesis of monomeric model compounds

2-Methoxy-4-(1-hydroxyethyl)phenol (**1a** in Scheme 1)[13]

To a solution of acetoguaiacone (7 g, 42 mmol) in 212 ml 56% ethanol, 3.5 g (93 mmol) of NaBH$_4$ are added in portions and afterwards stirred for 10 h at room temperature. Another portion of NaBH$_4$ (1 g, 26 mmol) is added and stirring is continued for additional 14 h. The reaction mixture was neutralized with CO_2 using small nuggets of dry ice introduced through a glass capillary with a wide diameter to prevent plugging. Then the mixture was diluted with 200 ml water and extracted six times with 150 ml Et$_2$O. The combined organic phases were dried over Na$_2$SO$_4$ and constricted to 200 ml under reduced pressure. The ethereal residue was transferred to a crystallization dish and left in a hood for slow crystallization which is necessary to prevent the formation of dimers. After separating the crude product from the mother liquor the crystals were dissolved in small amounts of ethyl acetate (the unsolvable dimers are filtered off) and precipitated by slowly adding n-hexane. Yield: 3.7 g (52%).

^{13}C NMR (75 MHz, CDCl$_3$): 146.61 (*C*-3), 144.98 (*C*-4), 137.93 (*C*-1), 118.32 (*C*-6), 114.15 (*C*-5), 107.99 (*C*-2), 70.33 (*C*-α), 56.00 (OMe), 25.09 (*C*-β)

1,2-Dimethoxy-4-(1-hydroxyethyl)benzene (1b)

Synthesis was accomplished analogous to 4-(1-Hydoxyethyl)-guaiacol starting from 1 g (5.55 mmol) 3,4-Dimethoxyacetophenon, 1.42 g (37.5 mmol) NaBH$_4$ and 150 ml abs. ethanol. After chromatographic purification (silica gel, ethyl acetate) of the crude product 0.87 g (4.77 mmol; 86%) of colorless crystals were obtained (m.p. 32-34°C).

4-(1-Ethoxy-ethyl)-2-methoxy-phenol

Isolation by column chromatography (SiO$_2$, eluent: CH$_2$Cl$_2$)

R$_f$ (SiO$_2$; CH$_2$Cl$_2$): 0.26

^{1}H NMR (300.1 MHz, CDCl$_3$) δ = 1.19 (t, 3 H, ^3J = 7.0 Hz, OCH$_2$C*H*$_3$), 1.43 (d, 3 H, ^3J = 6.5 Hz, β-H), 3.35 (q, 2 H, ^3J = 7.1 Hz, OC*H*$_2$CH$_3$), 3.91 (s, 3 H, OCH$_3$), 4.34 (q, 1 H, ^3J = 6.5 Hz, α-H), 5.56 (s, 1 H, ArOH), 6.83 (m, 3 H, ArH).

^{13}**C NMR** (75.5 MHz, CDCl$_3$): 146.69 (*C*-3), 144.85 (*C*-4), 136.10 (*C*-1), 119.24 (*C*-6), 113.98 (*C*-5), 108.19 (*C*-2), 77.54 (*C*-α), 63.62 (O*C*H$_2$CH$_3$), 55.80 (OMe), 24.15 (*C*-β), 15.32 (OCH$_2$*C*H$_3$)

Synthesis of the dimeric model compounds

The preparation of the dimeric β-*O*-4 lignin model compounds 2-(2,6-dimethoxy-phenoxy)-1-(4-hydroxy-3-methoxy-phenyl)-propane-1,3-diol **(5a)** and 2-(2,6-dimethoxy-phenoxy)-1-(3,4-dimethoxy-phenyl)-propane-1,3-diol **(5b)** is described elsewhere.[13,14]

Please print Scheme 1 here

HPLC analysis was performed with a Dionex system (P580 pump, GINA 50 autosampler,) running with Chromeleon 4 software. Detector: UVD340U diode detector. Column: Agilent; done with an Agilent Eclipse XDB-C18, Injection volume: 10 μl, Flow: 0.8 ml · min^{-1}, Gradient program: 0% eluent A → 95% eluent A (0 min → 15 min), 95% eluent A (15 min → 18 min), 0% eluent A (18 min → 20 min), Detection wavelength: 280 nm; Eluent A: 100% MeCN; Eluent B: 100% water.

GCMS analysis (GC 6890N / MSD 5973B): Fused silica HP-5ms (30 m, 0.25 mm, 25 μm), helium total flow 27.5 ml · min^{-1} (46.9 kPa), column flow 0.9 ml · min^{-1}; inlet temperature 230°C; injection 0.2 μl in splitless mode; temperature program 50°C (5 min), 10°C · min^{-1} to 280°C (20 min). Ionization was performed in EI mode at 70 eV. Data were acquired and processed with the Agilent Chemstation software.

RESULTS AND DISCUSSION

Formation of quinone methides and their impact on the reactivity of model compounds

Lignin is a comparatively low molecular, irregular polymer which consists of (substituted) 4-propylphenol (H), 4-propyl-2-methoxyphenol (G) and 4-propyl-2,6-dimethoxyphenol (S) building blocks which are interconnected by various types of linkages. Amongst them β-*O*-4, α-*O*-4 and cyclic α-*O*-4 / β-5' linkages are the dominating bonding sequences accounting for about 70% of all linkages between the above-mentioned principal lignin building units. The overall amount of these three types of linkages largely affects the reactivity of lignin in particular under alkaline conditions. If involved in the formation of β-*O*-4, α-*O*-4 and cyclic α-*O*-4 / β-5' linkages the phenol groups in H-, G- and S-units are no longer "free" but converted into less reactive aryl alkyl ethers or esters. This type of cross-linking, in turn, leads to fundamental differences in reactivity between lignin moieties where the hydroxyl group became part of a cross-link and those that carry a "free" phenolic OH group in *para*-position to the alkyl side chain, as only the latter have the ability to form quinone methides.

2-Methoxy-4-(1-hydroxyethyl)phenol (apocynol, **1a**) that feature this ability was shown to react under the experimental conditions (50% aq. ethanol, 120-160°C) to 4-(1-ethoxyethyl)-guaiacol (**3a**) and subsequently to 4-vinylguaiacol (**4a**, Scheme 2).

Please print Scheme 2 here

Even though three reaction pathways are likely, the significantly different conversion rates of the model compounds **1a** and **1b** evidenced that the reaction of apocynol proceeds via the intermediary formation of the quinone methide **2**. The latter can be stabilised either by reacting with ethanol to α-ethyl ether **3a** or by a [1,7]-sigmatropic proton shift yielding 4-vinylguaiacol (**4a**). The α-ethyl ether **3a** was shown to be the main product in the temperature

range of up to 160°C and only a further increase of temperature (200°C) and prolongation of reaction time (3 hours, *cf.* Figure 4) favours the onward reaction and formation of the elimination product **4a** as the dominating product. Thus we concluded that the stabilisation of the quinone methide **2** is rather accomplished by addition of ethanol than by a [1,7]-sigmatropic proton shift, at least up to about 160°C.

Figure 1 shows the decrease of the apocynol concentration for different temperatures. The data reveal that a) the conversion rate of **1a** is strongly temperature-dependent and that b) a certain amount of the educt **1a** is still present in all reaction mixtures even after longer reaction times being indicative for an equilibrium reaction.

Please print Figure 1 here

The exponential decay of the apocynol concentration $c_{[1a]}$ over the experimental time period t (Figure 2, left) along with the linear correlation between log $c_{[1a]}$ and t (Figure 2, right) evidenced that the conversion of apocynol **1a** under the studied conditions follows a first-order rate law.

The formation of 4-(1-ethoxyethyl)-2-methoxy-phenol that was isolated from the reaction mixture by column chromatography (*cf.* materials and methods section) follows the same kinetics however the linear correlation range is here limited to shorter reaction times due to the increasingly favored onward-reaction to 4-vinylguaiacol (data not shown). The existence of a first-order rate law for the equilibrium between **1a** and **3a** in the temperature range of 120°C to 160°C was additionally confirmed by the kinetics of the back reaction, i.e. the formation of apocynol from 4-(1-ethoxyethyl)-2-methoxy-phenol (**3a**) at 130°C (Figure 2, right).

Please print Figure 2 here

4-(1-Hydoxyethyl)-veratrol (compound **1b**) that differs from **1a** only by methylation of the phenolic OH group, reacts in a similar way as its phenolic counterpart. However, **1b** was confirmed to feature a significantly reduced reactivity when compared to **1a.** Even at 170°C, a half-time of only 52 min was estimated for 4-(1-hydoxyethyl)-veratrol (**1b**, *cf.* Figure 3, left) whereas that of 4-(1-hydoxyethyl)-guaiacol (**1a**) is less than 10 minutes. The distinctly lower reactivity of **1b** is supposed to be due to its etherified phenolic OH group that prevents **1b** from forming an intermediary quinone methide as mentioned above. Other than for the conversion of apocynol the formation of the ethyl ether **3b** is proposed to follow a zero-order rate law as the experimentally determined half-life of 52 min was found to be in good agreement with the theoretical value of 50 min. The theoretical half-time for a first-order rate law would have been 32 min. The observed differences in the kinetics are highly likely due to the fact that the formation of 4-(1-ethoxyethyl)-guaiacol **3b** proceeds *via* a nucleophilic substitution of the hydroxyl group in C_α position of **1b** instead *via* an intermediary quinone methide (**2**) as it is assumed to be the case for **1a**. The different reaction mechanisms are also the reason that only in the reaction mixtures of **1a**, smaller amounts of by-products were found which are most likely formed in competitive reactions of **2a** with **1a**, ethanol, and water (back reaction).

The comparatively low activation energy for the conversion of **1a** to **3a** of $\Delta G^\ddagger$ of 53±7.6 $kJ \cdot mol^{-1}$ as derived from the Arrhenius plot (Figure 2, left) disfavors a radical reaction course in the studied temperature range. Homolytic cleavage of C-H or C-C bonds would require activation energies considerably higher than 100 $kJ \cdot mol^{-1}$ whereas only comparatively low activation energies are required for heterolytic cleavage of polar covalent bonds, in particular when energetically stable products are formed.

The assumption that the conversion of apocynol to compound **3a** does not proceed via a radical state was further experimentally supported by studying the formation of carbonyl groups of a cellulose sample (cotton linters, CL) in relation to its change in molecular weight and

hence amount of reducing end groups. Figure 3 (right) shows that the joint treatment of apo-cynol with cotton linters under Organosolv conditions (50% v/v aqueous ethanol, 160°C) causes typical moderate cellulose degradation.

Please print Figure 3 here

The weight-average molecular weight dropped from 126.1 kg · mol^{-1} to 85.5 kg · mol^{-1} after 120 min of pulping time which is very similar to a cotton linters sample treated without the addition of **1a** (92.4 kg · mol^{-1}). The carbonyl group content increased during the treatment for pure CL from 9.2 to 16.02 mmol · kg^{-1} and in the presence of apocynol up to 16.4 mmol · kg^{-1}. This corresponds in a coarse approximation the theoretical number of reducing end groups that was calculated from M_n, the number-average molecular weight. Assuming that the reaction would proceed via a radical intermediate, a pronounced oxidation of cellulose and considerable increase of carbonyl groups would have been observed. As this was not the case (also in a repetition of the experiment using finely ground pine kraft lignin instead of **1a** (see black dots in Figure 3, right), we conclude that the α-ethyl ether derivative **3a** is formed from **1a** either by nucleophilic substitution (both S_N1 and S_N2 is possible as the solvent reacts as a nucleophile) at the C_α position of the alkyl side chain or via an intermediary quinone methide (**2**, Scheme 2). The intermediary formation of the latter is highly likely under Organosolv conditions due to the slight acidic conditions caused by the free phenolic OH groups of both the model compound **1a** and lignin.

GC/MS analysis of the reaction mixtures obtained after treating the monomeric model compounds **1a** and **1b** in 50% (v/v) aqueous ethanol at 200°C for three hours (*cf*. Figure 4) confirmed that even under rather harsh conditions radical species seems not to play a major role. This was concluded from the fact that the monomers participating in the above-described

equilibrium (**3a**/**4a** and **3b**/**4b** *cf.* Scheme 2) were found to be the main products for both the phenolic and the non-phenolic model compound.

Please print Figure 4 here

However, the occurrence of radical side reactions in the conversion of **1a** cannot be ruled out, as a smaller amount of dimers was found to be present in the reaction mixture too. Except for the apocynol dimer (m/z 300.5, M^+) the participation of radical species in the formation of at least two of these compounds, namely the 5,5'-coupling product 3,3'-dimethoxy-5,5'-divinyl-biphenyl-2,2'-diol (m/z 298.3, M^+) and the 5,7-dihydro-dibenzo[c,e]oxepine derivative (m/z 316.4) is likely.

A similar picture was obtained when treating the dimeric β-*O*-4 model compounds 2-(2,6-dimethoxy-phenoxy)-1-(4-hydroxy-3-methoxy-phenyl)-propane-1,3-diol (**5a**, see Scheme 1) and 2-(2,6-dimethoxy-phenoxy)-1-(3,4-dimethoxy-phenyl)-propane-1,3-diol (**5b**) in 50% (v/v) aqueous ethanol at 180°C for 20 minutes. The insert of Figure 5 shows the high stability of the β-*O*-4 linkage under Organosolv conditions when the phenolic groups are "blocked" by etherification or esterification (**5b**). In contrast, many different reaction products were obtained for the phenolic counterpart **5a.** This is in good agreement with the results published by Kishimoto and Sano who studied the conversion of the structurally related dimeric model compound guaiacylglycerol-β-guaiacyl ether under high-boiling solvent conditions, i.e. treatment with 1,3- or 1,4-butanediol at 180°C for 20 minutes.[6] Based on the product fingerprint (GC/MS) and the confirmation of the peak assignment by column chromatography and subsequent NMR studies, they concluded that the cleavage of β-*O*-4 linkages is mainly accomplished by homolytic degrading reactions.

Please print Figure 5 here

The results of our study support these findings to some extent as no significant amounts of Hibbert's ketones could be found in the chromatograms of the reaction mixtures which would be at least indicative for an acidolytic cleavage of the β-*O*-4 linkages. On the other hand, neither the formation of typical radical coupling products nor that of oligomers as reported by the above-mentioned authors could be confirmed. Furthermore, the structure of some of the assigned dimers rather support a similar chemistry as suggested for apocynol, i.e. the formation of an intermediary quinone methide and its subsequent conversion into the corresponding a-ethyl ethers and α-β-unsatured compounds.

The effect of scCO$_2$ on the delignification process

The above described experiments using the model compounds **1a** were repeated in a 0.2 l high-pressure autoclave to study the influence of supercritical carbon dioxide on the reaction pathway and the kinetics of the respective reactions. The experiments conducted at 140°C, 160°C and 180°C confirmed the positive correlation between temperature and conversion rate of the educt (*cf.* Figure 6).

Please print Figure 6 here

But this increase is only of minor relevance compared with a much stronger degradation effect in presence of super critical carbon dioxide. As indicated in Figure 6, the degradation rate at 140°C with scCO$_2$ present is even faster than the reaction rate at 180°C without scCO$_2$. The order of this reaction was estimated as first order. The calculation of the Arrhenius activation

energy gave significantly lower activation energy for this reaction when $scCO_2$ was applied. For the reaction without $scCO_2$, an E_A of 68.9 kJ $\cdot$ mol^{-1} could be determined, which is in good agreement with literature. Shantalov and Pereira reported 64 kJ $\cdot$ mol^{-1} for the initial delignification of fibre crop under Organosolv condition but higher values for bulk and residual lignin fractions.[15] Macfarlane et al. found the activation energy for delignification during Organosolv pulping dependent of the ethanol concentration with 52 kJ $\cdot$ mol^{-1} for 70% ethanol and 84kJ $\cdot$ mol^{-1} for 35% ethanol in water. Interpolation to 50% (v/v) aqueous ethanol as used in the present study, gives an activation energy of 70 kJ $\cdot$ mol^{-1} which is in accordance with the determined value.[16] Under $scCO_2$ catalysis, the activation energy is much lower and could be determined with 42.0 kJ $\cdot$ mol^{-1}, which is approximately 40% less than under uncatalyzed conditions.

HPLC analysis of the samples revealed that the overall degradation reaction of the model substance apocynol (**1a**) is a combination of two consecutive reactions. The first step is the transformation of apocynol into 4-(1-ethoxyethyl)-2-methoxy-phenol (**3a**) via a *para*-chinone methide (*p*QM) intermediate (**2**) (*cf.* Scheme 2). The second step is the degradation into 2-methoxy-4-vinylphenol (**4a**) through cleavage of one molecule ethanol according to a pseudo-first-order rate law (*cf.* Figure 7). Also in this case the stabilization proceeds via the chinone methide (**2**) and not through a [1,7]-sigmatropic proton shift as indicated in Scheme 2. This fact became evident as 2-methoxy-4-vinylphenol (**4a**) only appears as a succession product of 4-(1-ethoxyethyl)-2-methoxy-phenol (**3a**).

Please print Figure 7 here

Although $scCO_2$ was found to enhance the degradation of the model compound in first place, it surprisingly leads to a slowdown of the subsequent transformation of 4-(1-ethoxyethyl)-2-

methoxy-phenol (**3a**) into 2-methoxy-4-vinylphenol (**4a**). Even the effect of temperature almost vanished. The presence of $scCO_2$ also effects the zero order formation of the end product (**4a**). Although the final concentration is higher when $scCO_2$ is applied, the initial reaction rate is definitely higher when no $scCO_2$ is present.

Please print Figure 8 here

CONCLUSIONS

In this study it could be shown that apocynol reacts via a quinone methide intermediate which is stabilized by formation of an α-ethyl ether through addition of ethanol and not by a [1,7]-sigmatropic proton shift. This α-ethyl ether was also found to be the main product whereby higher reaction temperatures and longer reaction times cause 4-vinylguaiacol to become the dominating product. Replacement of the phenolic group in the model compounds by a methoxy group lead to a significantly reduced reactivity which can be explained with its inability to form the intermediary quinone methide. Methoxylated model compounds are transformed through nucleophilic substitution. This finding is of great importance for further studies with dimer model compounds. A radical reaction course was found to be unlikely as a matter of low activation energies and negligible formation of carbonyl groups in cellulose samples, even under harsh conditions.

Investigations towards the role of supercritical carbon dioxide during delignification were done using again apocynol as model compound. Kinetic studies with and without supercritical carbon dioxide at different temperatures revealed, that the use of supercritical carbon dioxide during the pulping process accelerates not only the decay of the model substance but also lowers the activation energy for this reaction distinctly. On the contrary it was shown that the

presence of super critical carbon dioxide only accelerated the transformation into the intermediate product but slowing down then formation of the end product. This can potentially be explained by a carbonate formation, stabilizing the reaction intermediate and causing a slower transformation. In addition to its aiding effects in biomass penetration these results would support the use of super critical carbon dioxide as an enhancer in an Organosolv pulping process aiming for maximum delignification by affecting this process in a direct manner. Deeper insights in the role of super critical carbon dioxide on the complex delignification process require pursuing investigations with dimeric model compounds containing a β-*O*-4 ether bond typical for the macromolecular structure of lignin which are currently underway.

REFERENCES

1. Clark J. H.; Budarin V.; Deswarte F. E. I.; Wilson A. J. Green chemistry and the biorefinery: a partnership for a sustainable future. Green Chem. **2006**, *8*, 853-860.

2. Kleinert T.; Tayenthal K. Ueber neuere Versuche zur Trennung von Cellulose und Inkrusten verschiedener Hoelzer. Angewandte Chemie **1931**, *44*, 788-791.

3. McDonough T.J. The chemistry of organosolv delignification. Tappi Journal **1993**, *76*(8), 186-193.

4. Oliet M.; Garcia J.; Rodriguez F.; Gilarranz M. A. Solvent effects in autocatalyzed alcohol-water pulping – Comparative study between ethanol and methanol as delignifying agents. Chem. Eng. J. **2002**, *87*, 157-162.

5. Kishimoto, T.; Sano Y. Delignification Mechanism during High-Boiling Solvent Pulping. Part 1. Reaction of Guaiacylglycerol Ether. Holzforschung **2001**, *55*, 611-616.

6. Kishimoto, T.; Sano, Y. Delignification Mechanism during High-Boiling Solvent Pulping. Part 2. Homolysis of Guaiacylglycerol-β-Guaiacyl Ether. Holzforschung **2002**, *56*, 623-631.

7. Kishimoto, T.; Sano, Y. Delignification Mechanism during High-Boiling Solvent Pulping. Part 3. Structural Changes in Lignin Analyzed by 13C-NMR Spectroscopy. Holzforschung **2003**, *57*, 602-610.

8. Kishimoto, T.; Sano, Y. Delignification Mechanism during High-Boiling Solvent Pulping. Part 4. Effect of Reducing Sugar on the Degradation of Guiacylglycerol-β-guiacyl Ether. J. of Wood Chem. and Technol. **2003**, *23*, 233-248.

9. Kishimoto, T.; Sano, Y. Delignification Mechanism during High-Boiling Solvent Pulping. Part 5. Reaction of Nonphenolic β-O-4 Model compounds in the Presence and Absence of Glucose. J. of Wood Chem. and Technol. **2003**, *23*, 279-292.

10. Kishimoto, T.; Sano, Y. Delignification Mechanism during High-Boiling Solvent Pulping. Part 6. Changes in lignin structure analyzed by 1H-13C correlation 2-D NMR spectroscopy. Holzforschung **2004**, *58*, 355-362.

11. Gao M.; Xu F.; Li S.; Ji X.; Chen S.; Zhang D. Effect of SC-CO_2 pretreatment in increasing rice straw biomass conversion. Biosystems Engineering **2010**, *106,* 470-475.

12. Pasquini D.; Pimeta M. T. B.; Ferreira L. H. Sugar cane bagasse pulping using supercritical CO_2 associated with co-solvent 1-butanol/water. J. Supercrit. Fluid. **2005**, *34*, 125-131.

13. Adler E.; Delin A.; Miksche G.E. Synthese des Isoeugenolglykol-β-(2-methoxyphenyl)-aethers. Acta Chem. Scand. **1966**, *20*(4), 1035-1037.

14. Nakatsubo, F.; Sato, K.; Higuchi, T. Synthesis of guaiacylglycerol- β-guaiacyl ether. Holzforschung **1975**, *29*(5), 165.

15. Shatalov, A.A.; Pereira, H. Kinetics of organosolv delignification of fibre crop *Arundo donax L.* Ind. Crops and Prod. **2005**, *21*, 203-210

16. Macfarlane, A.L.; Farid, M.M.; Chen, J.J.J. Kinetics of delignifications using a batch reactor with recycle. Chem. Eng. and Proc. **2009**, *48*, 854-870

Figure captions

Scheme 1: Monomeric (**1a**: 2-Methoxy-4-(1-hydroxyethyl)phenol; **1b**: 4-(1-Hydoxyethyl)-veratrol) and dimeric model compounds (**5a**: 2-(2,6-dimethoxy-phenoxy)-1-(4-hydroxy-3-methoxy-phenyl)-propane-1,3-diol; **5b**: 2-(2,6-dimeth-oxy-phenoxy)-1-(3,4-dimethoxy-phenyl)-propane-1,3-diol) used in the current study.

Scheme 2: Equilibrium reactions of the monomeric model compounds **1a** and **1b** under Organosolv conditions (ethanol/water, 50/50 (v/v), 120-200°C).

Figure 1: Time-dependent conversion of apocynol (**1a**, left) in aqueous ethanol at 120-160°C (left). The linear correlation of $\ln[c_0/c]$ and reaction time evidences a first-order rate law (right).

Figure 2: Arrhenius plot and activation energy $\Delta G^{\ddagger}$ for the conversion of apocynol under Organosolv conditions in the temperature range of 120-160°C (left); Kinetics of the back reaction of 4-(1-ethoxy-ethyl)-2-methoxyphenol (**3a**) to apocynol at 130°C (**1a**; right).

Figure 3: Degradation of the non-phenolic model compound **1b** is much slower and follows a zero-order rate law (left). Carbonyl contents (red) and weight-average molecular weight of cotton linters (blue) jointly treated with apocynol or wood (black dots) under Organosolv conditions (50% (v/v) aqueous ethanol, 160°C, right).

Figure 4: GC/MS-analysis of the reaction mixtures obtained after treating the monomeric model compounds **1a** and **1b** in 50% (v/v) aqueous ethanol at 200°C for three hours.

Figure 5: Gas chromatograms of the reaction mixtures obtained after treating the β-*O*-4-type model compounds **5a** and **5b** (insert) in 50% (v/v) aqueous ethanol at 180°C for 20 min.

Figure 6: Kinetics of apocynol (**1a**) degradation at different temperatures with and without scCO$_2$

Figure 7: Formation and transformation of the reaction intermediate 4-(1-ethoxy-ethyl)-2-methoxyphenol (**3a**)
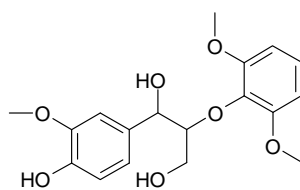
Figure 8: Formation of the end product 2-methoxy-4-vinylphenol (**4a**) at different temperatures with and without scCO$_2$.
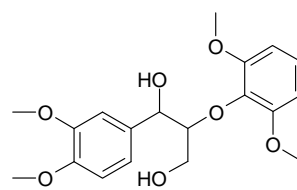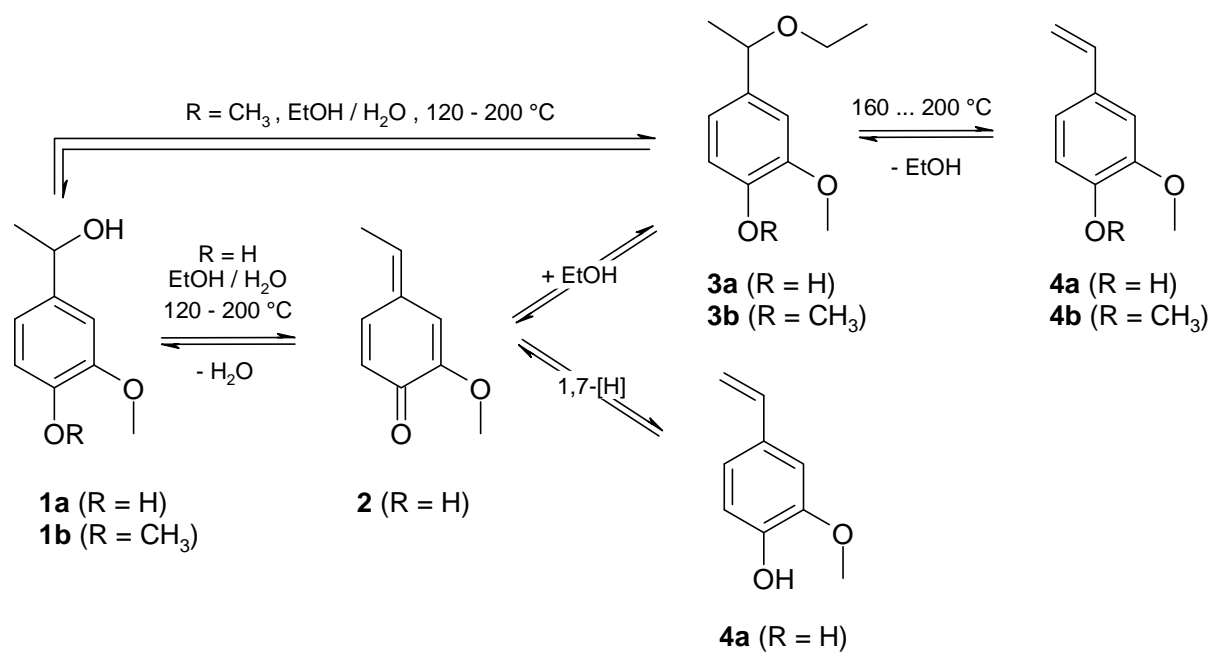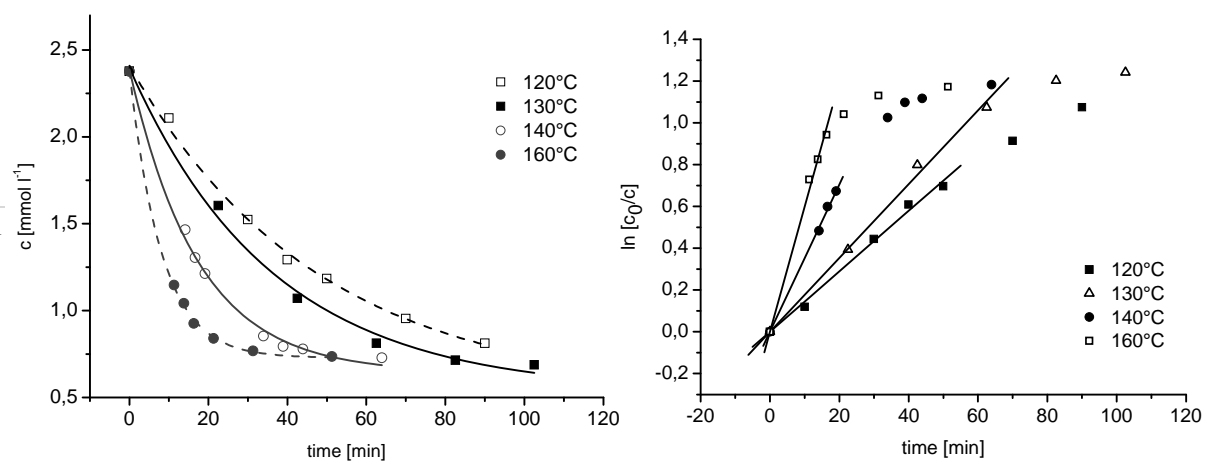
1a   **1b**   **5a**   **5b**

Scheme 1

R = CH$_3$, EtOH / H$_2$O , 120 - 200 °C

160 ... 200 °C

- EtOH

R = H
EtOH / H$_2$O
120 - 200 °C

- H$_2$O

+ EtOH

1,7-[H]

OH

1a (R = H)
1b (R = CH$_3$)

2 (R = H)

3a (R = H)
3b (R = CH$_3$)

4a (R = H)
4b (R = CH$_3$)

4a (R = H)
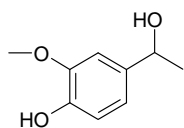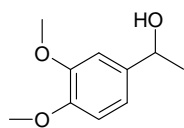
Scheme 2
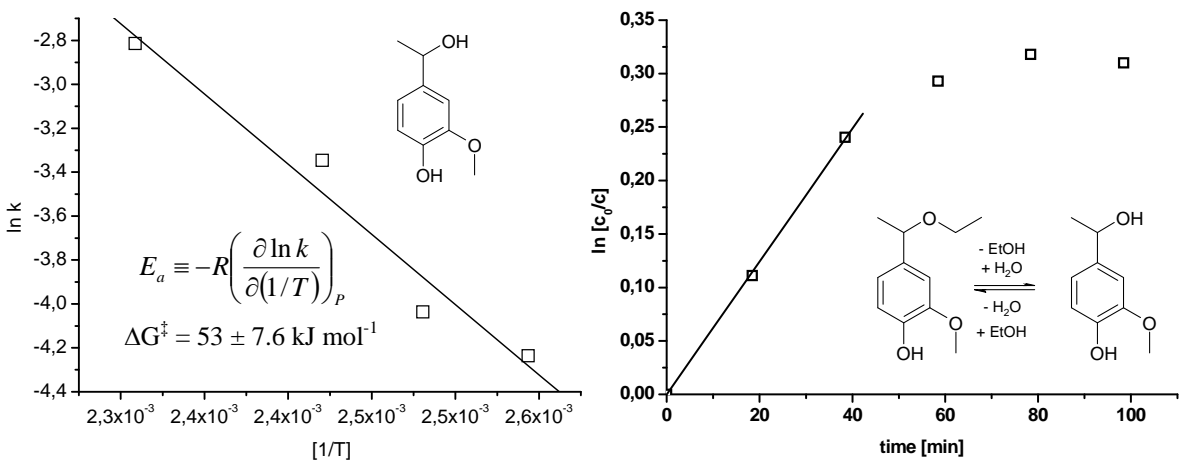
Figure 1

Figure 2
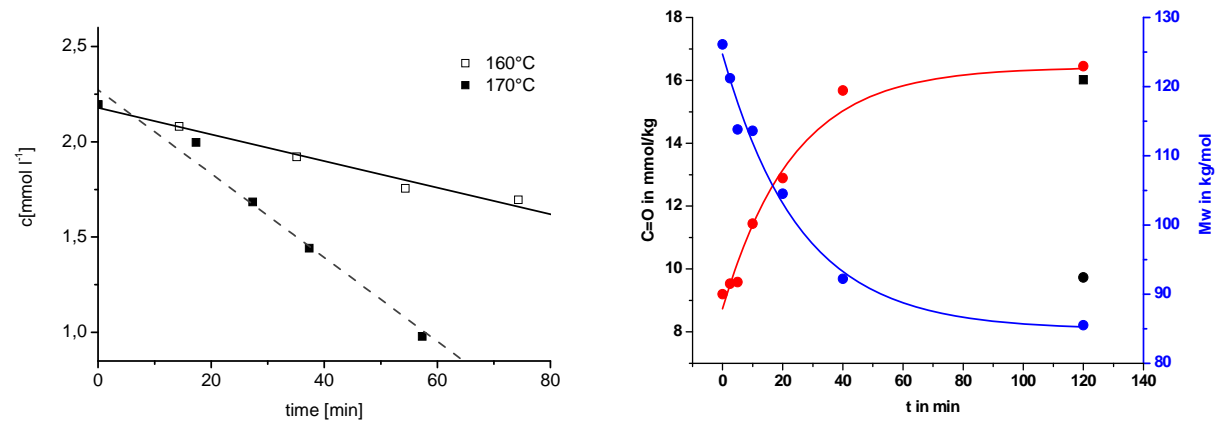
Figure 3
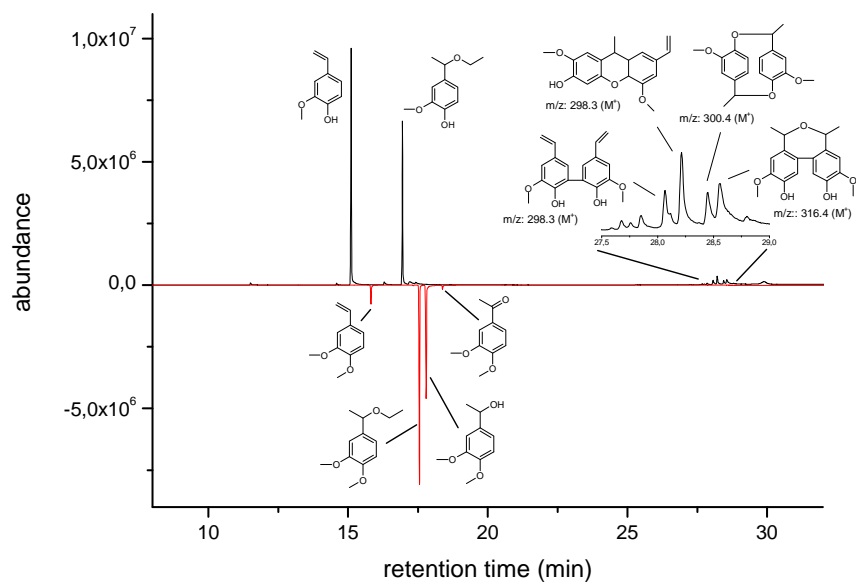
Figure 4
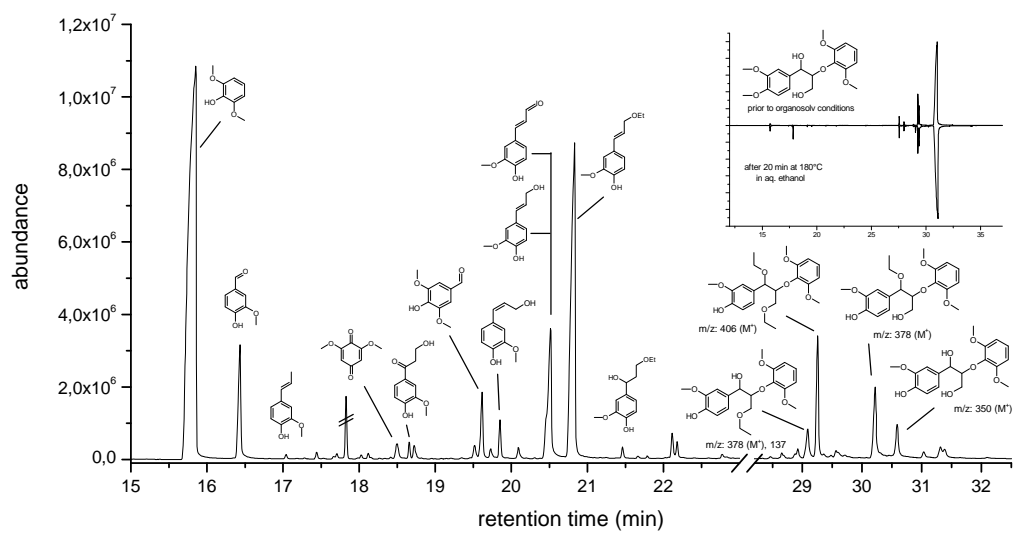
Figure 5
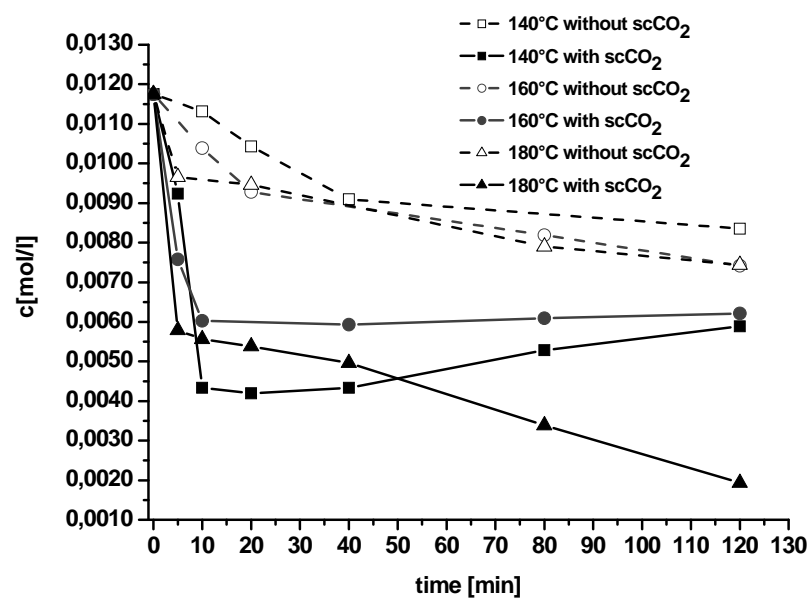
Figure 6
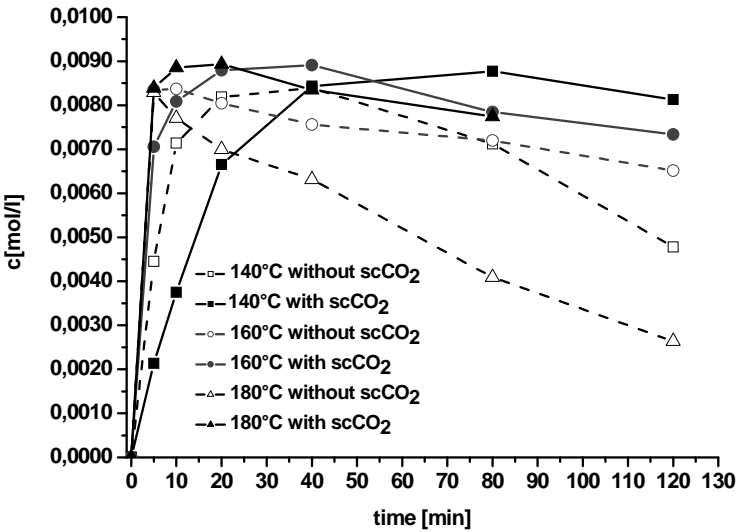
Figure 7
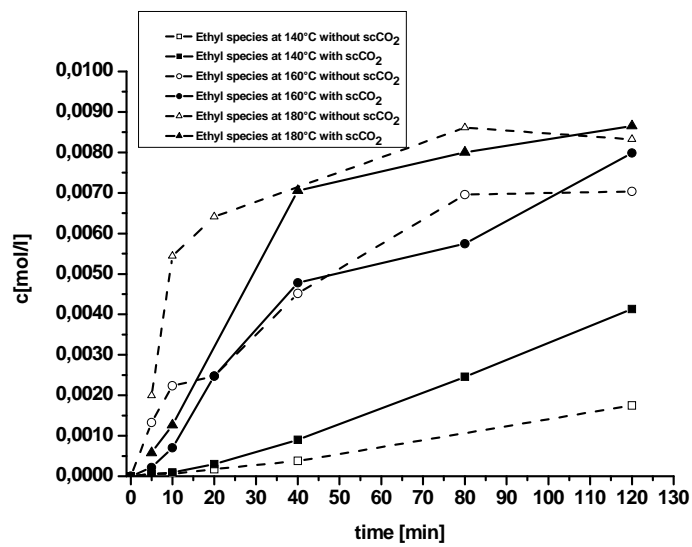
Figure 8

Ionic Liquid Pretreatment of Pine Wood Chips for Reduced Energy Input during Grinding

Michael Schrems,[a,b] Agnieszka Brandt,[b,c] Jason P. Hallett,[b] Richard J. Murphy,[c,d] Antje Potthast,[a] Michael Ray,[d] Thomas Rosenau,[a] Tom Welton[b,c]*

[a] Christian-Doppler-Laboratory "Advanced cellulose chemistry and analytics", Department of Chemistry, University of Natural Resources and Life Sciences, A-1190 Vienna, Austria

[b] Department of Chemistry, Imperial College London, London, SW7 2AZ, UK

[c] The Porter Alliance, Imperial College London, London, SW7 2AZ, UK

[d] Division of Biology, Imperial College London, London, SW7 2AZ, UK

* To whom correspondence should be addressed, t.welton@imperial.ac.uk

Abstract

Ionic liquids are of great interest as potential solvents/reagents for the production of fuels and chemicals from lignocellulosic biomass. Attention has focussed particularly on the pretreatment of finely ground lignocellulose to make the cellulose accessible to enzymatic hydrolysis. Any biomass process invariably requires a reduction in the size of the harvested biomass by chipping and grinding to make it more amenable to chemical or biological treatment. This paper addresses the question of whether addition of the ionic liquid should occur before or after grinding the feedstock. It is demonstrated that significant energy reductions can be achieved in the grinding of pine wood chips (8 mm x 7 mm x 7 mm) if the ionic liquid is added before the grinding operation. It is shown that this due to the lubricating properties of the ionic liquids and not to physico-chemical modifications of the biomass by the ionic liquids.

Keywords

Ionic liquid, biomass, biorefinery, grinding, wood.

Introduction

Ionic liquids are becoming increasingly important as potential process solvents.[1] An area of particular interest in the last few years has been their potential use as solvents for biomass processing.[2] For lignocellulose, most studies in this area have focused on the use of pre-ground flour. It has been demonstrated that the size of the wood particles affects the

dissolution rates, since smaller particles give a greater surface area to volume ratio.[3] However, it has also been noted that the energy consumption for grinding wood to flour could be a process-limiting cost for any lignocellulose based fuel and/or chemicals production.[4] Our investigations of the action of ionic liquids on pine wood chips (10 x 10 x 5 mm) showed considerable swelling of the chips with some ionic liquids, but not with others.[5] They also showed partial dissolution of the biomass, particularly with strongly hydrogen-bonding anions. These observations led us to consider the possibility that such ionic liquid treated wood chips may be more amenable to grinding due to their swollen nature and hence the energy requirement for the grinding could be significantly reduced. Herein we report our investigations of this possibility.

Experimental

Materials

All reagents were purchased from Aldrich, unless otherwise stated. 1-Methylimidazole (Acros Organics) and 1-butylimidazole were distilled under vacuum from potassium hydroxide. 1-Chlorobutane was distilled over P_2O_5. Ethyl acetate, acetonitrile, toluene and dichloromethane were supplied by VWR and dried using an Innovative Technologies solvent drying tower system. Ethanol, DMSO, dimethylsulfate, silver nitrate, and lithium *bis*(trifluoromethylsulfonyl)imide were used as received. High-boiling silicone oil (Acros Organics) and perfluoropolyether (PFPE, Fomblin Y 06/6) were also used as received. All ionic liquids were prepared using literature procedures (see ESI).[6]

Preparation of wood chips

Pine (*Pinus radiata*) sapwood was obtained from a 15 year old tree harvested at Silwood Park, Ascot, in June 2008. All wood was taken from material sawn from the main trunk. Pine sapwood specimens of dimensions 8 mm x 7 mm x 7 mm were prepared. Specimens were stored air-dried at normal temperature and room humidity in the laboratory. The moisture content of the pine wood was 9% on oven-dry basis.

Ionic liquid pretreatment of wood chips

A Schlenk flask was used as a soaking apparatus. Eight wood chips (*ca*. 1.25 g) were placed into the Schlenk flask which was then sealed with a rubber septum. The flask was evacuated for 60 s to ensure maximum liquid uptake into the voids. 5 ml of the liquid was injected through the septum with a syringe and the evacuated flask heated to the treatment temperature and kept under these conditions during the whole treatment period. Subsequently the Schlenk flask was flushed with nitrogen, the wood specimens were removed from the liquid and placed on a paper towel to remove any liquid on the surface.

Grinding experiments

An A10 Yellow Line analytical grinder from IKA Works Inc. was connected to a PM300 three phase power analyzer from Voltech *via* a plug-socket adapter especially built for this application. This adapter was toggled between the two devices to provide three inputs for the power analyzer, which integrated the energy consumption over the time of the grinding. To achieve reproducible results, it was necessary to run the grinder empty prior to each grinding series. In each experiment, eight cubes were placed in the grinder containing a compartment to reduce the working volume of the grinding chamber. Water cooling was applied at all times to avoid overheating of the grinder. The energy was integrated over a period of 30 seconds as this was long enough to transform the wood chips into fine powder. The integration time was set to one minute, and the grinding process started after 30 seconds had elapsed. This avoided uncertainties arising from combining the integration onset and the beginning of the grinding, as the first seconds of grinding contribute most towards the energy consumption. Each experiment was replicated three times because it was found that the error limits were the same as when replicated seven times. Unfortunately, it was impossible to separate the ionic liquid and the biomass by sieving, so the size of the wood particles could not be determined.

Results and discussion

The aim of this study is to compare the energy demand for grinding wood chips with or without an ionic liquid pretreatment. For this purpose the effect of different ionic liquids and other process variables on the energy demand were investigated (Table 1). The pine wood was used in air-dried form and thus contained a substantial amount of water. This was because rigorous drying would require a substantial additional energy input, which would be an undesirable cost for any biomass pretreatment process. Since this leads to the introduction of considerable amounts of water to the ionic liquids these were also not dried prior to use. It should be noted that these values vary widely with the ionic liquids used and particularly with the selection of the ionic liquid's anion.[7]

Our previous work on the effects of different ionic liquids on pine wood chips demonstrated that using different anions led to different degrees of swelling and softening of the chips.[5] We hypothesised that we could expect a similar affect on the energy required to grind the chips. Hence, we selected three ionic liquids for this study each of which give different degrees of swelling of pine wood chips and varying ability to dissolve cellulose. 1-Butyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide ($[C_4C_1im][NTf_2]$) does not induce swelling and there is no evidence for dissolution of cellulose; 1-butyl-3-methylimidazolium hydrogensulfate ($[C_4C_1im][HSO_4]$) gives some pine wood swelling; it extracts and dissolves lignin and enhances the accessibility of the cellulose fraction to hydrolases, but is not able to dissolve cellulose; 1-butyl-3-methylimidazolium acetate ($[C_4C_1im][MeCO_2]$) gave significant swelling of pine chips and can dissolve cellulose and

lignocellulosic materials very effectively. Our studies to date suggest that the effect of changing the ionic liquid cation on the swelling of pine chips is secondary to the anion effect and so the cation was kept constant throughout this experiment.

Initial experiments with the empty grinder under the conditions described above showed an energy consumption of 0.87 Wh (Table 1) over the measured 30 seconds. The energy demand to grind untreated wood chips was 1.28 Wh giving an additional energy requirement of 0.41 Wh. It is this value that we are comparing our pretreated wood results to, e.g. an energy requirement of 1.08 Wh would indicate a saving of approximately 50% in comparison to the air-dry wood sample.

The first three tests used pine chips that had been treated either with $[C_4C_1im][MeCO_2]$, $[C_4C_1im][HSO_4]$ or $[C_4C_1im][NTf_2]$ at 90°C for 1 h to induce swelling where possible. The energy input necessary to grind these samples was reduced by 59%, 66% and 52% respectively. These savings are substantial and potentially process significant. Interestingly, there was very little difference between the samples treated with different ionic liquids. A relationship between the degree of swelling or between the ability to dissolve cellulose and the energy saving could not be observed. Otherwise we would have not seen a significant energy reduction for the chips treated with the inert $[C_4C_1im][NTf_2]$.

Table 1. The energy consumption for grinding of pine wood chips.

Liquid	Pretreatment conditions	Energy consumption	Energy saving relative to dry wood (%).
Empty	N/A	0.872	N/A
Empty grinder / silicone oil	N/A	0.892	N/A
Dry wood	N/A	1.275	N/A
$[C_4C_1im][NTf_2]$	90°C, 1h	1.069	52
$[C_4C_1im][HSO_4]$	90°C, 1h	1.011	66
$[C_4C_1im][MeCO_2]$	90°C, 1h	1.039	59
Silicone oil	90°C, 1h	0.997	69
PFPE Fomblin Y 06/6	90°C, 1h	1.003	68
DMSO	90°C, 1h	1.217	15
Organosolv	90°C, 1h	1.149	31

[C$_4$C$_1$im][MeCO$_2$]	90°C, 18h	0.939	84
Silicone oil	90°C, 18h	0.939	84
[C$_4$C$_1$im][MeCO$_2$]	120°C, 18h	0.959	79
Silicone oil	120°C, 18h	0.961	78

Ionic liquids have been demonstrated to be excellent lubricants.[8] To test whether the power savings were due to lubrication by the ionic liquid, we repeated the grinding experiments using wood chips that had been treated with other widely used lubricants. They were selected to be hydrophobic and so unable to interact with the wood matrix. High-boiling silicone oil gave an energy reduction of 69% and perfluoropolyether gave an energy reduction of 68%. Neither of these induced any swelling of the wood chips.

To further confirm that the energy savings were not the consequence of the breakdown of the wood by the ionic liquids pretreatment, we compared the energy demand of grinding pine chips treated with either [C$_4$C$_1$im][MeCO$_2$] or silicone oil for a longer time. Our previous results showed that longer ionic liquid pretreatment resulted in greater breakdown of the wood's structure.[5] For wood chips treated at 90°C for 18 hours, the [C$_4$C$_1$im][MeCO$_2$] and the silicone oil chips gave almost identical results, both with a reduced energy demand of approximately 84%. Increasing the temperature from 90°C to 120°C was also tested. A treatment of pine wood chips at 120°C with [C$_4$C$_1$im][MeCO$_2$] after approximately 18 hours caused a significant degradation of the treated wood chips to the point that some of the cubes actually split apart. Surprisingly, even for this sample, the energy requirement was only slightly lower than the one obtained after 18 hours at 90°C. We observed that, although the surface of the wood chips was softened, their interior was less affected. An experiment with silicone oil under identical conditions gave an energy reduction of 79% which is again almost identical to the 78% achieved with [C$_4$C$_1$im][MeCO$_2$]. This suggests that increased lubrication may be responsible for the additional energy savings. The improved lubrication seems to arise from greater physical penetration of the wood chip at the higher temperature by the lubricating liquids and not from modifications of the structure or the linkages of the wood. The improved penetration at higher temperature is likely due to the reduced viscosity of these liquids at the more elevated temperatures.

To exclude the possibility that the reduction of grinding energy was simply the result of wetting the sample, we repeated these measurements with a 1:1 water ethanol mixture, the solvent used for Organosolv pulping, which gave an energy reduction of 31%, and the polar organic solvent DMSO, which reduced the energy demand by only 15%. While these liquids, which are not noted to be effective lubricants, provided some energy reduction, this is not of the order of savings achieved by either the ionic liquids or the other well-known lubricants.

Finally, we excluded the possibility that the energy saving was due to these liquids simply lubricating the grinding mechanism of the instrument, with the observation that the

empty grinder with added silicone oil gave almost the same values as for the completely empty grinder. These tests showed that the observed effect is not caused by simply lubricating the rotor blades as no additional reduction of the grinding energy demand could be observed.

Conclusions

Ionic liquids can significantly reduce the energy required for grinding of pine wood. This behaviour arises from their tribological properties and not from chemical or structural modification of the wood. These results suggest that any ionic liquid based wood pretreatment aimed at producing either fuels or chemicals will be more energy and, therefore, cost efficient, if the ionic liquid is added to the wood before the grinding.

Acknowledgements

References

[1] (*a*) J. P. Hallett and T. Welton, *Chem. Rev.*, 2011, **111**, 3508. (*b*) P. Wasserschied and T. Welton (eds.), *Ionic liquids in synthesis*, VCH Wiley, Weinheim, 2nd ed., 2007; (c) Plechkova, N. V.; Seddon, K. R. *Chem. Soc. Rev.* **2008**, *37*, 123.

[2] M. Mora-Pale, L. Meli, T. V. Doherty, R. J. Linhardt, J. S. Dordick, *Biotech. Bioeng.*, 2011, **108**, 1229.

[3] N. Sun, M. Rahman, Y. Qin, M. L. Maxim, H. Rodriguez and R. D. Rogers, *Green Chem.*, 2009, **11**, 646; I. Kilpeläinen, H. Xie, A. King, M. Grainstrom, S. Heikkinen, D. Argyropoulos, J. Agric. Food Chem. 2007, **55**, 9142.

[4] (a) J. Y. Zhu, X. Pan, R. S. Zalesny Jr., *Appl. Microbiol Biotechnol.*, 2010, **87**, 847; (b) W. Zhu, J. Y. Zhu, R. Gleisner, X. J. Pan, *Bioresour. Technol.*; 2010, **101**, 2782.

[5] A. Brandt, J. P. Hallett, D. J. Leak, R. J. Murphy, T. Welton, *Green Chem.*, 2010, 12**,** 672.

[6] T. Wells, J. P. Hallett, C. K. Williams, and T. Welton, *J. Org. Chem.*, 2008, **73**, 5585.

[7] L. Cammarata, S. G. Kazarian, P. Salter, T. Welton, *Phys. Chem. Chem. Phys.*, 2001, **3**, 5192.

[8] (a) C. Ye, W. Liu, Y. Chen, L. Yu, *Chem. Comm.*, **2001**, 2244; (b) I. Minami, *Molecules*, 2009, **14**, 2286; (c) F. Zhou, Y. Liang, W. Liu, *Chem. Soc. Rev.*, 2009, **38**, 2590.

Instrumentation

Liquid secondary ion mass spectrometry (LSIMS) was performed on a Micromass AutoSpec Premier. Electrospray ionisation (ESI) mass spectra were recorded on a Micromass LCT Premier instrument. ^{1}H-NMR and ^{13}C-NMR spectra (proton-decoupled) were recorded with a Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm (relative to tetramethylsilane) and coupling constants are given in Hz. Elemental analysis was carried out by the London Metropolitan University Service.

Synthesis of [C$_4$C$_1$im]Cl:
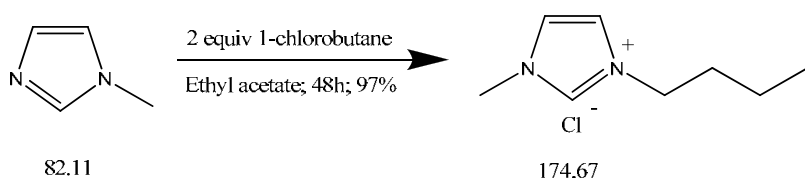
136.2 ml (1.71 mol) of freshly distilled 1-methylimidazole and 150 ml of dry ethyl acetate were placed in a 1000 ml three neck flask under nitrogen atmosphere equipped with a 500 ml dropping funnel. 360 ml (3.42 mol) of freshly distilled 1-chlorobutane was added drop wise at room temperature under extensive stirring. The mixture was heated to max. 80°C for about 48 h. The solution was cooled to room temperature to obtain the desired compound as white crystals with a pink hue. The solid was washed with EtOAc and recrystallized from acetonitrile. The supernatant was removed under vacuum. This step was repeated until the product was obtained as white crystals. The white solid was dried under vacuum overnight to get the desired product in 45% yield (134.7g).

^{1}H NMR, δ_H (400MHz, d$_6$-DMSO); 0.90 (3H, t, *J* 7.3 Hz, NCH$_2$CH$_2$CH$_2$C*H*$_3$), 1.26 (2H, m, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.77 (2H, m, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 3.88 (3H, s, NCH$_3$), 4.19 (2H, t, *J* 7.3 Hz, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 7.78 (1H, dd, *J* 1.7 Hz, C(5)H), 7.85 (1H, dd, *J* 1.7 Hz, C(4)H), 9.41 (1H, s, C(2)H).

^{13}C NMR, δ_C (100MHz, d$_6$-DMSO); 13.74 (NCH$_2$CH$_2$CH$_2$CH$_3$), 19.21 (NCH$_2$CH$_2$CH$_2$CH$_3$), 31.80 (NCH$_2$CH$_2$CH$_2$CH$_3$), 36.15 (NCH$_3$), 48.88 (NCH$_2$CH$_2$CH$_2$CH$_3$), 122.72, 124.03 (C(5)H, C(4)H), 137.12 (NCN)

Synthesis of [C$_4$C$_1$im][(CF$_3$SO$_2$)$_2$N]:
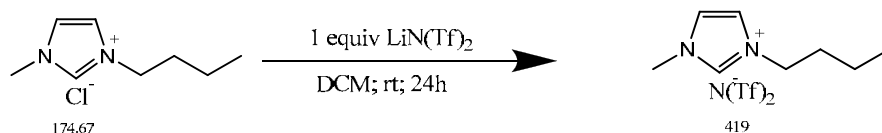

60.0 g (0.34 mol) of [C$_4$C$_1$im]Cl and 103.3 g (0.35 mol) of lithium bis(trifluoromethylsulfonyl)imide were placed in a 500 ml two neck round flask inside the glove box. 100 ml of dry dichloromethane were added and stirred for 24 h at room temperature under nitrogen atmosphere. Once the reaction was finished, the solid was allowed to settle and separated from the DCM by canula filtration. This solid was further rinsed with freshly distilled DCM (2x100 ml). All liquid fractions obtained from filtration were mixed together and the DCM evaporated to obtain the crude product. The oil was diluted with dry DCM and washed with small aliquots (20 ml) of distilled water to remove chloride impurities. The organic solution was washed until halide free as indicated by the AgNO$_3$ test. The solvent was removed in a rotary evaporator and the crude oil stirred with active coal for one day before filtering through a short pad of neutral alumina and finally dried under high vacuum to obtain a colorless oil in 57% yield (81.2 g).

^{1}H NMR, δ_H (400MHz, d$_6$-DMSO); 0.91 (3H, t, J 7.3 Hz, NCH$_2$CH$_2$CH$_2$CH$_3$), 1.28 (2H, m, NCH$_2$CH$_2$CH$_2$CH$_3$), 1.78 (2H, m, NCH$_2$CH$_2$CH$_2$CH$_3$), 3.86 (3H, s, NCH$_3$), 4.17 (2H, t, J 7.3 Hz, NCH$_2$CH$_2$CH$_2$CH$_3$), 7.67 (1H, dd, J 1.7 Hz, C(5)H), 7.74 (1H, dd, J 1.7 Hz, C(4)H), 9.10 (1H, s, C(2)H).

^{13}C NMR, δ_C (100MHz, d$_6$-DMSO); 13.45 (NCH$_2$CH$_2$CH$_2$CH$_3$), 19.15 (NCH$_2$CH$_2$CH$_2$CH$_3$), 31.75 (NCH$_2$CH$_2$CH$_2$CH$_3$), 36.01 (NCH$_3$), 48.95 (NCH$_2$CH$_2$CH$_2$CH$_3$), 121.52 (CF$_3$), 122.64, 124.01 (C(5)H, C(4)H), 136.92 (NCN)

Synthesis of [C₄C₁im][MeSO₄]:


Synthesis of [C$_4$C$_1$im][MeSO$_4$]:
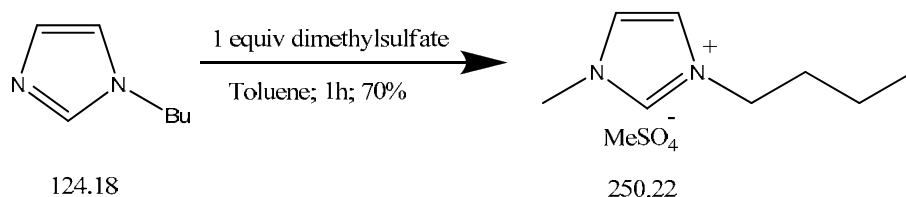
87 g (0.7 mol) n-butylimidazole was mixed with 130 ml toluene and the mixture cooled to 0°C. 67 ml (0.7 mol) dimethylsulfate was added drop-wise while stirring. The stirring was continued for 1 hour at room temperature. The top phase was decanted and the lower phase was washed three times with 50 ml of toluene. The ionic liquid was dried under vacuum. The product was a colourless, viscous liquid with a yellow hue in 98% yield (171.52 g).

^{1}H NMR, δ_H (400MHz, d$_6$-DMSO); 0.88 (3H, t, *J* 7.3 Hz, NCH$_2$CH$_2$CH$_2$C*H*$_3$), 1.25 (2H, m, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 1.76 (2H, m, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 3.41 (3H, s, *H*$_3$C-O-S), 3.86 (3H, s, NC*H*$_3$), 4.18 (2H, t, *J* 7.3 Hz, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 7.72 (1H, dd, *J* 1.7 Hz, C(5)H), 7.80 (1H, dd, *J* 1.7 Hz, C(4)H), 9.13 (1H, s, C(2)H).

^{13}C NMR, δ_C (100MHz, d$_6$-DMSO); 13.65 (NCH$_2$CH$_2$CH$_2$*C*H$_3$), 19.19 (NCH$_2$CH$_2$*C*H$_2$CH$_3$), 31.80 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 36.08 (N*C*H$_3$), 48.91 (N*C*H$_2$CH$_2$CH$_2$CH$_3$), 53.38 (s, *H*$_3$*C*-O-S), 122.72, 124.03 (C(5)H, C(4)H), 137.05 (N*C*N)

*Synthesis of [C$_4$C$_1$im][HSO$_4$]:*
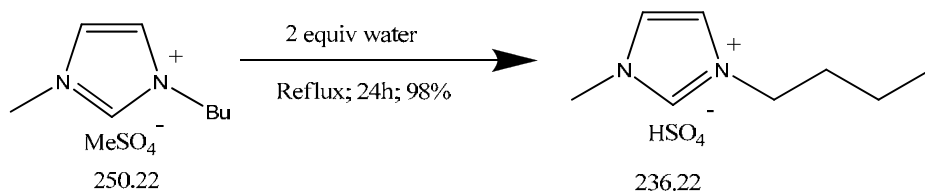
125 g (0.5 mol) [C$_4$C$_1$im][MeSO$_4$] were mixed with 18 ml distilled water in a round-bottomed flask with vertical Graham condenser connected to a horizontal Liebig condenser. The mixture was heated to reflux (150°C). The Graham condenser was

cooled to 65°C using a temperature-controlled circulator. The Liebig condenser was cooled with room temperature water. The aqueous solution was heated under reflux for 24 h. Most water was removed with the rotary evaporator and the ionic liquid dried under vacuum at 45°C to obtain the desired compound in 93% yield (110.2 g).

^{1}H NMR, δ_H (400MHz, d$_6$-DMSO); 0.85 (3H, t, J 7.3 Hz, NCH$_2$CH$_2$CH$_2$CH_3), 1.22 (2H, m, NCH$_2$CH$_2$CH_2CH$_3$), 1.75 (2H, m, NCH$_2$CH_2CH$_2$CH$_3$), 3.86 (3H, s, NCH$_3$), 4.17 (2H, t, J 7.3 Hz, NCH_2CH$_2$CH$_2$CH$_3$), 7.73 (1H, dd, J 1.7 Hz, C(5)H), 7.81 (1H, dd, J 1.7 Hz, C(4)H), 9.01 (1H, s, HSO$_4$), 9.20 (1H, s, C(2)H).

^{13}C NMR, δ_C (100MHz, d$_6$-DMSO); 13.70 (NCH$_2$CH$_2$CH$_2$CH$_3$), 19.20 (NCH$_2$CH$_2$CH$_2$CH$_3$), 31.80 (NCH$_2$CH$_2$CH$_2$CH$_3$), 36.10 (NCH$_3$), 48.87 (NCH$_2$CH$_2$CH$_2$CH$_3$), 122.74, 124.06 (C(5)H, C(4)H), 137.10 (NCN)

Synthesis of [C$_4$C$_1$im]Br:

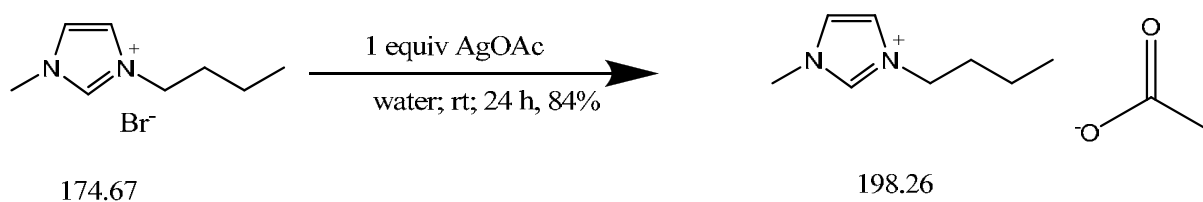

82.11   218.04
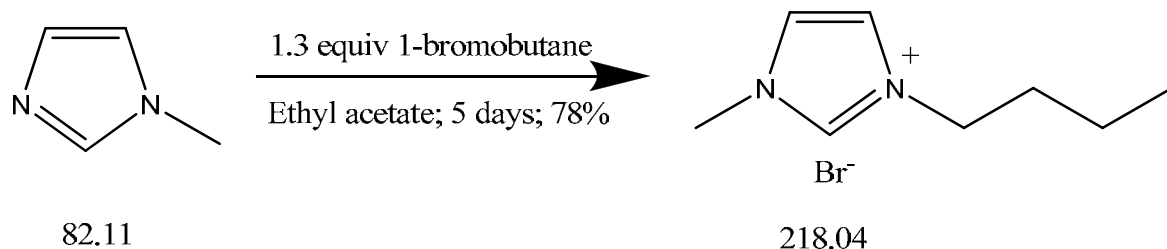
1-Methylimidazole (100 ml, 1.27 mol) was mixed with 100 ml ethyl acetate. 1-Bromobutane (143 ml, 1.33 mol) was added dropwise. The mixture was stirred at room temperature overnight. The temperature was raised to 35°C, the emulsion stirred for 4 days and then cooled to -20°C to crystallise the product. The product was recrystallised in acetonitrile; the white crystals were dried and stored in the glove box until further use (yield: 78.4%)

^{1}H-NMR (400 MHz, DMSO-d$_6$) δ: 9.34 (1H, s, CH-2), 7.87 (1H, s, CH-4), 7.79 (1H, s, CH-5), 4.20 (2H, t, N-CH_2-), 3.88 (3H, s, N-CH_3), 1.77 (2H, m, N-CH$_2$-CH_2-), 1.25 (2H, m, N-CH$_2$-CH$_2$-CH_2-), 0.89 (3H, t, N-CH$_2$-CH$_2$-CH$_2$-CH_3) ppm.

$^{13}C\{^1H\}$-NMR (100 MHz, DMSO-d$_6$) δ: 137.00 (s, C-2), 124.02 (s, C-4), 122.72 (s, C-5), 48.88 (s, N-CH_2(CH$_2$)$_2$CH$_3$), 36.24 (s, N-CH_3), 31.84 (s, N-CH$_2$$CH_2CH_2CH_3$), 19.21 (s, N-(CH$_2$)$_2$$CH_2CH_3$), 13.75 (s, N(CH$_2$)$_3$$CH_3$) ppm.

Elemental analysis (calc.): %C=43.75 (43.85), %H=6.87 (6.90), %N=12.71 (12.78).

Synthesis of [C$_4$C$_1$im][MeCO$_2$]:

174.67   1 equiv AgOAc / water; rt; 24 h, 84%   198.26

[C$_4$C$_1$im]Br (130.2 g, 0.594 mol) and silver acetate (99.7 g, 0.597 mol) was transferred into a 500 ml conical flask. The flask was covered with aluminium foil to reduce photo degradation of silver bromide. 250 ml distilled water was added and the suspension stirred overnight. The yellowish precipitate was filtered off. An aqueous 2 mol/L solution of [C$_4$C$_1$im]Br was added dropwise. The addition was stopped when precipitate formation ceased and a subsequent test for silver ions with dilute HCl was negative. The solution was placed in the continuous extractor and extracted with ethyl acetate for 16 h. The water was removed with the rotary evaporator and the ionic liquid dried to completion using high vacuum at 60°C (Yield: 84.8%)

^{1}H-NMR (400 MHz, DMSO-d$_6$) δ: 10.17 (1H, s, CH-2), 7.91 (1H, s, CH-4), 7.83 (1H, s, CH-5), 4.20 (2H, t, N-CH_2-), 3.88 (3H, s, N-CH_3), 1.75 (2H, m, N-CH$_2$-CH_2-), 1.58 (3H, m, $^-$O$_2$C-CH_3), 1.22 (2H, m, N-CH$_2$-CH$_2$-CH_2-), 0.87 (3H, t, N-CH$_2$-CH$_2$-CH$_2$-CH_3) ppm.

^{13}C{^{1}H}-NMR (100 MHz, DMSO-d$_6$) δ: 173.59 (s, COO$^-$),137.04 (s, C-2), 124.02 (s, C-4), 122.27 (s, C-5), 48.41 (s, N-CH$_2$(CH$_2$)$_2$CH$_3$), 35.76 (s, N-CH$_3$), 31.33 (s, N-CH$_2$$CH_2CH_2CH_3$), 18.74 (s, N-(CH$_2$)$_2$$CH_2CH_3$), 13.27 (s, N(CH$_2$)$_3$$CH_3$) ppm.

m/z (LSIMS$^+$): 139 (100%) [C$_4$C$_1$im]+, 337 (14%) [(C$_4$C$_1$im)$_2$CH$_3$CO$_2$]+. m/z (LSIMS$^-$): 59 (100%) [CH$_3$CO$_2$]$^-$, 119 (61%) [(CH$_3$CO$_2$)$_2$H]$^-$, 257 (68%) [(CH$_3$CO$_2$)$_2$(C$_4$C$_1$im)]$^-$, 455 (28%) [(C$_4$C$_1$im)$_2$(CH$_3$CO$_2$)$_3$]$^-$.

Elemental analysis (calc.): %C=60.63 (60.58), %H=9.13 (9.15), %N=13.96 (14.13).

MICHAEL SCHREMS curriculum vitae

PERSONAL DATA

Date of Birth: February 15, 1984

Nationality: Austrian

Marital Status: Married

E-mail: michael.schrems@boku.ac.at

Cell: +43 6502649350

EDUCATION

Oct 2008 – present

Department of Chemistry, BOKU

Dr. in Engineering Sciences
Supervisor: Prof. Antje Potthast; Prof. Thomas Rosenau, 3 year program
Green Refinery – Ionic Liquids a novel media for biomass processing

May 2009 – May 2011

Turku University of Applied Sciences, TUAS

MBA in General Management
Supervisor: Dr. Martin Stieger, MBA MPA
The U.S. Consumer Market: Successful marketing in a demographically changing America

Oct 2004 – June 2008

University of Vienna

Mag. of Natural Sciences in Chemistry
Supervisor: Prof. Wolfgang Kautek; Ass.-Prof. Günter Trettenhahn
Rotating disc electrode investigation of the heterogeneous electrochemistry in aprotic aluminium alkyl electrolytes

Sept 1998 – June 2003

Higher Federal Training and Research College for Chemical Industry, Vienna

Austrian Matura
Emphasis on practical chemical and biological sciences

RESEARCH EXPERIENCE

Nov 2008 – present

Department of Chemistry, BOKU

Full time research associate
Christian Doppler Laboratory for Advanced Cellulose Chemistry and Analytics

Oct 2010 – Jan 2011

Department of Chemistry, Imperial College London

Short Term Scientific Mission
Supervisor: Prof. Tom Welton
Characterization of cellulosic/ionic liquid films by atomic force microscopy

Dec 2007 – Oct 2008

Department of Physical Chemistry, University of Vienna

Full time engineering assistant
Supervisor: Prof. Wolfgang Kautek
Confidential

Nov 2006 – Jun 2007

Department of Physical Chemistry, University of Vienna

Part time scientific employee
Supervisor: Ass.-Prof. Günter Trettenhahn
Confidential

MICHAEL SCHREMS

curriculum vitae

AWARDS

2010   COST scholarship (Short Term Scientific Mission)

ADDITIONAL SKILLS & ACTIVITIES

Languages   German (native), English (fluent), Spanish (basic)

**Jan 2009
– May 2011**   Austrian National Bench Press Team
Participations: 2x European Championships (2009, 2010)
                1x World Championships (2011)

PARTICIPATION AT SYMPOSIA

Jul 2009, 15th European Carbohydrate Symposium
Poster Presentation & abstract – 'Studies towards the reaction behavior of common 1-alkyl-3-methylimidazolium-based ionic liquids as media for carbohydrate chemistry'

Aug 2010, 11th European Workshop on Lignocellulosics and Pulp
Poster Presentation & abstract – 'Dissolution of renewable materials in ionic liquids for biorefinery analytics'

Mar 2011, 2011 AIChE Spring Meeting & 7th Global Congress on Process Safety
Oral Presentation & abstract – 'Organosolv revisited – Biomass valorization with new perspectives'

Jun 2011, RR2011, International Conference "Renewable Wood and Plant Resources: Chemistry, Technology, Pharmacology, Medicine"
Oral Presentation & abstract – 'Biomass processing in ionic liquids'

REFERENCES

Prof. Antje Potthast
Department of Chemistry, University of Natural Resources and Life Sciences, Vienna, Austria
antje.potthast@boku.ac.at

Prof. Thomas Rosenau
Department of Chemistry, University of Natural Resources and Life Sciences, Vienna, Austria
thomas.rosenau@boku.ac.at

Prof. Tom Welton
Department of Chemistry, Imperial College London, London, UK
t.welton@imperial.ac.uk

Vienna, 05.07.2011