IEA Bioenergy Workshop

Task 33

Novel gasification with bio-thermochemical coupling technology

Prof. Beibei Yan

School of Environmental Science and Engineering

Tianjin University

2022.10.19

CONTENTS

1 Brief introduction of background

The Paris Agreement and double carbon

United Nations | Climate Action

To tackle climate change and its negative impacts, world leaders at the UN Climate Change Conference (COP21) in Paris reached a breakthrough on 12 December 2015: the historic Paris Agreement.

International policy

The Paris Agreement

The Paris Agreement provides a durable framework guiding the global effort for decades to come. It marks the beginning of a shift towards a net-zero emissions world. Implementation of the Agreement is also essential for the achievement of the Sustainable Development Goals.

China policy

Double carbon target

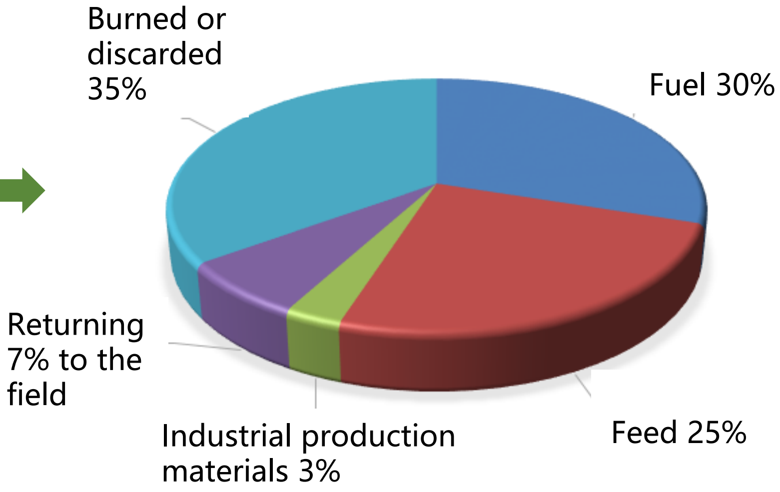
General debate of the 75th session of the United Nations General Assembly on 22 September 2022.
"China will enhance national independent contribution, adopt more effective policies and measures, strive to reach the peak of carbon dioxide emissions by 2030, and strive to achieve carbon neutrality by 2060."

Biomass solid waste scale in China

Agroforestry biomass

- High moisture content
- High solids content
- High organic matter content
- Rich in nutrient elements
- Relatively high calorific value

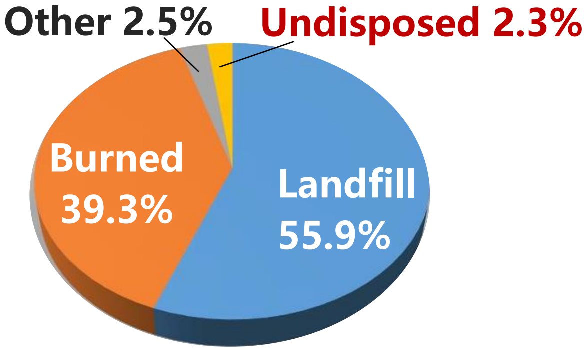
In 2020, the total was 3.047 billion tons



Industrial biomass waste

- Concentrated production with large yields
- Multiple sources
- High moisture content
- Heavy metal elements

In 2020, the total was 650 million tons



- Biomass is the best choice for developing sustainable clean energy because of its rich nutrition and relatively high calorific value;
- In China, biomass is diversified and abundant in yield, but its utilization efficiency is relatively low;
- Then there is an urgent need for effective disposal means to reduce environmental risks

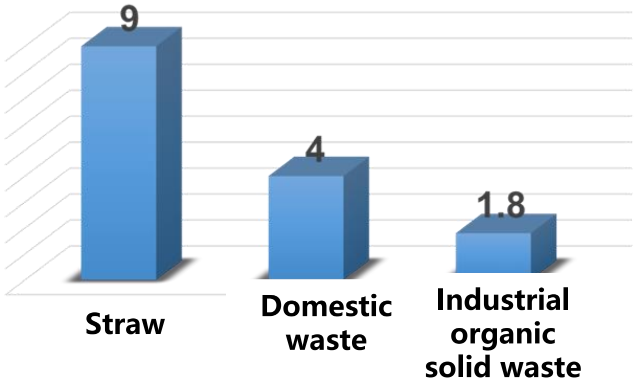
Environmental risks from bio-wastes

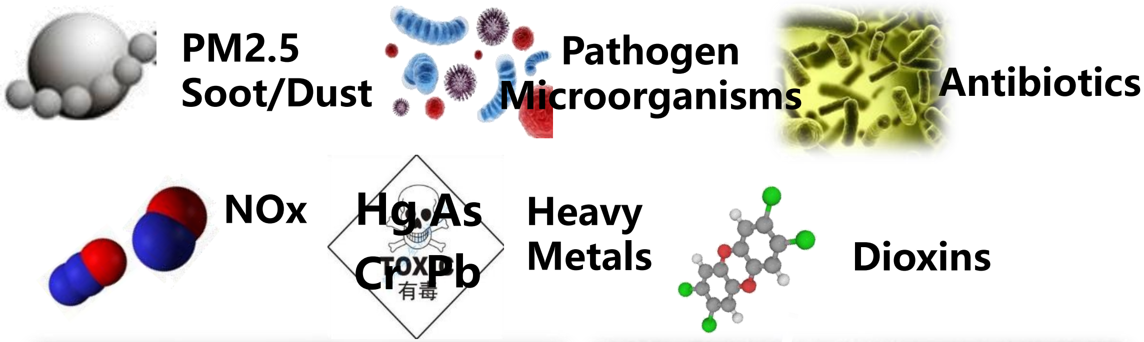
Biomass solid waste (agricultural sources) simple combustion is repeatedly prohibited

Neighborhood avoidance effect" in MSW incineration

How to deal with biomass solid waste (industrial sources)

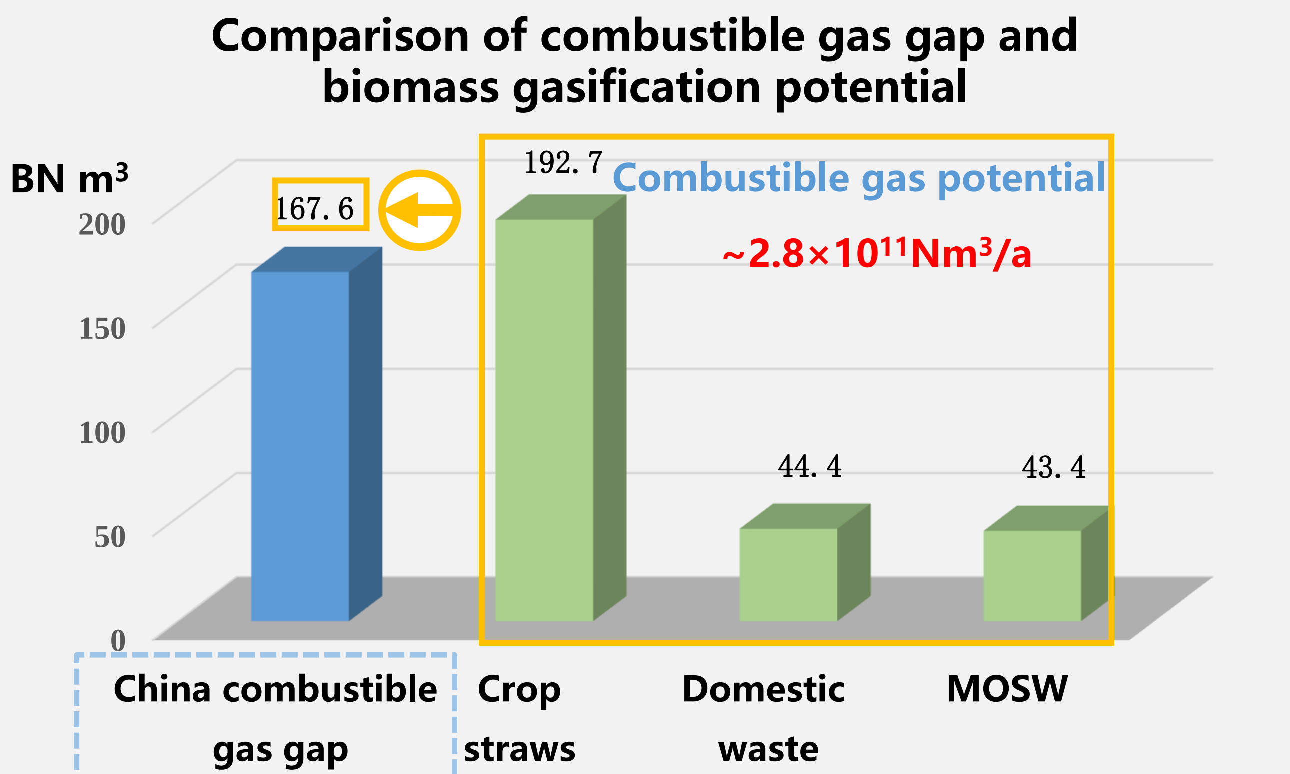
Annual production of biomass solid waste (Billion tons/year)





Clean treatment of biomass solid waste is of great significance to environmental management and pollutant reduction

Fuel gas demand for China



Proportion of gap: 45.1%

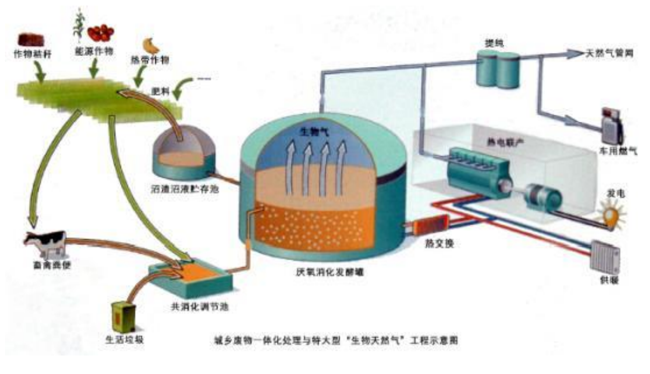
Estimated with 2021 gas demand data

Biomass gasification can convert organic components into bio fuel gas under anaerobic or hypoxic conditions; Gasification will solve the problems of biomass/wastes gathering and incineration, reduce environmental pollution.

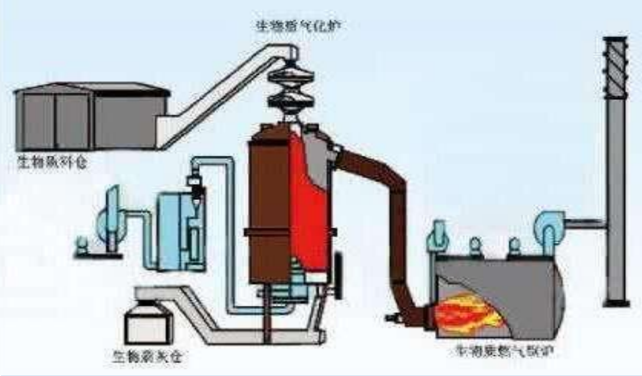
The gasification of biomass solid waste effectively supplements the fuel gas gap while environmental pressure, which promotes the realization of the “double carbon” target in China

Novel gasification concept

Biomass conversion technology



Anaerobic digestion (AD)



Gasification (GS)

Advantages and disadvantages

High heat value methane
Good environmental benefits

Long process cycle
Low conversion efficiency
Residue problem of biogas residue

Short process cycle
Rapid production of oil, gas and carbon

Low gases quality
Limited applications
Blocked pipes by tar

Coupling process

Integration advantage

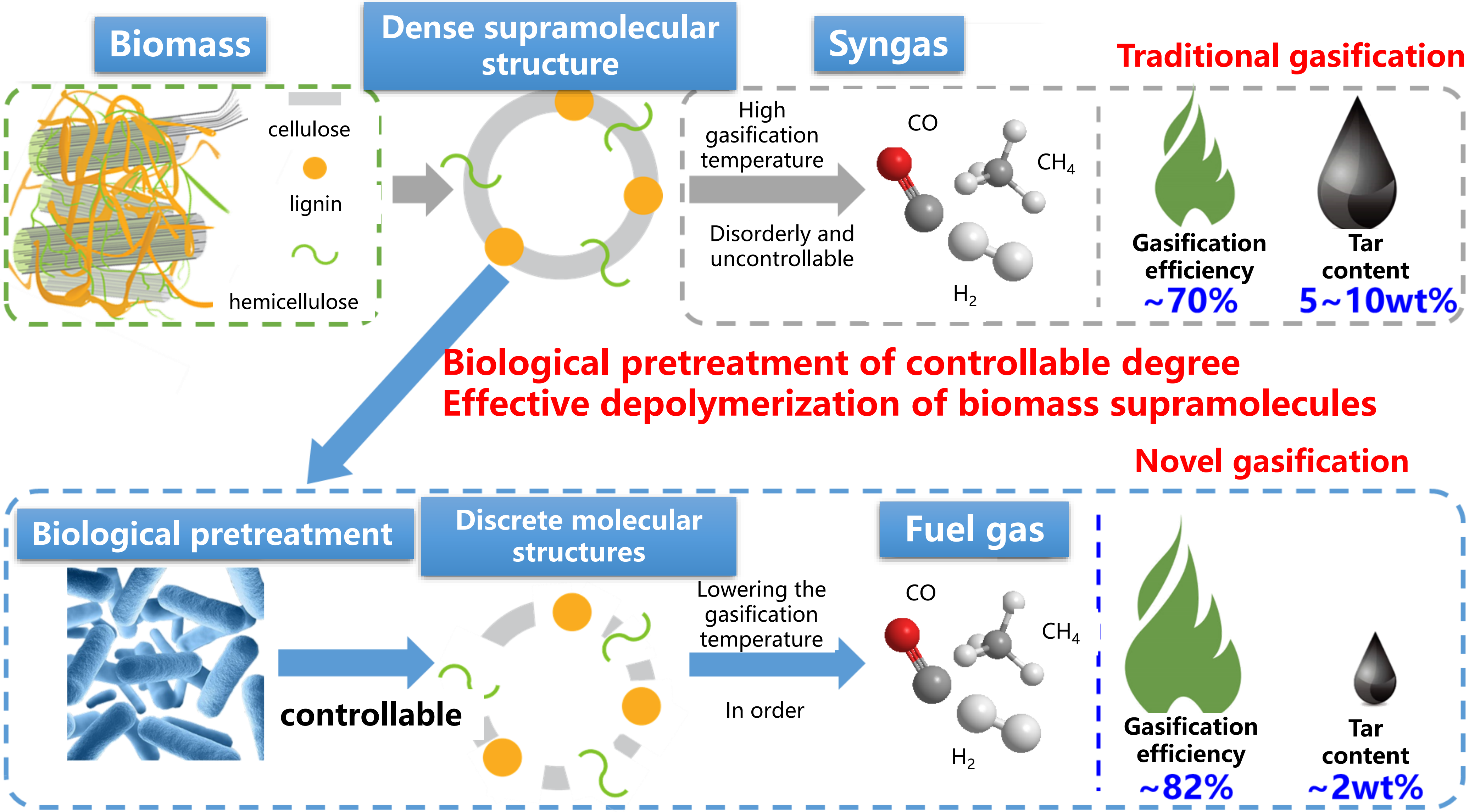
Conversion efficiency is improved

Biogas residue is further utilized

The tar content is reduced

Gas applications are extended

Theoretical basis for novel gasification



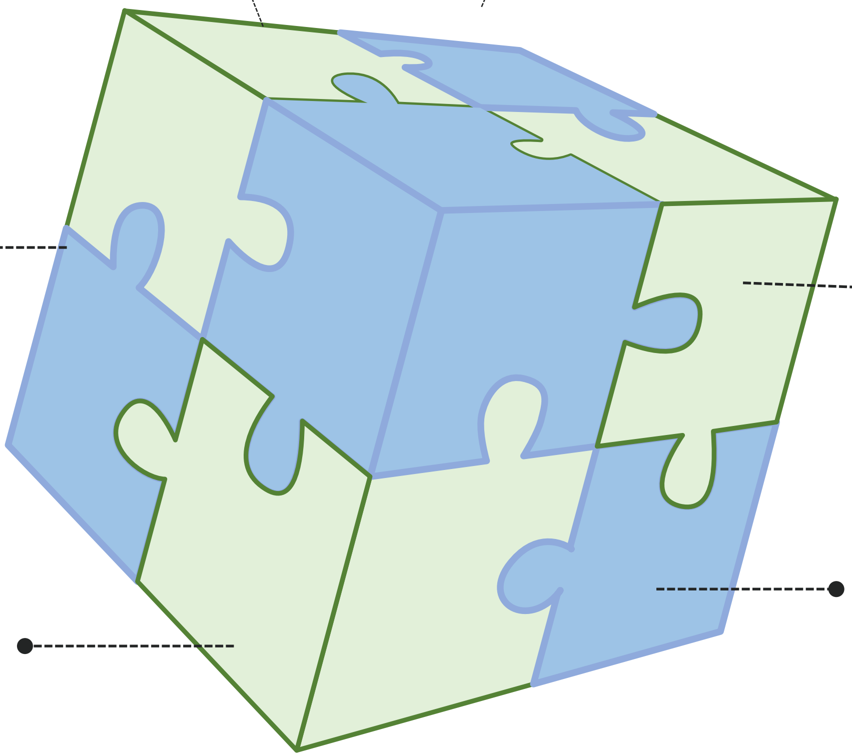
Novel gasification, which combines anaerobic fermentation with traditional gasification, has become a more promising way to utilize biomass energy

Crucial scientific issues

How much volatile matter is consumed by AD?

Can AD intensity have a different effect on biomass GS?

How to achieve maximum energy recovery through AD and GS?



GS potential of biogas residue

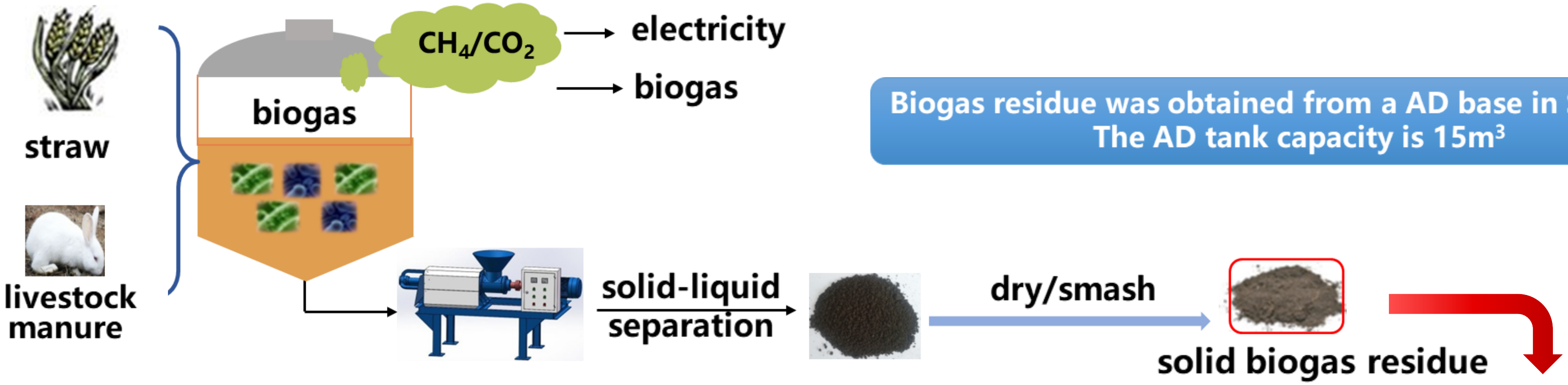
Effects of AD on GS

Novel process as controllable AD-GS

2 Research updates

2.1 GS potential of biogas residue

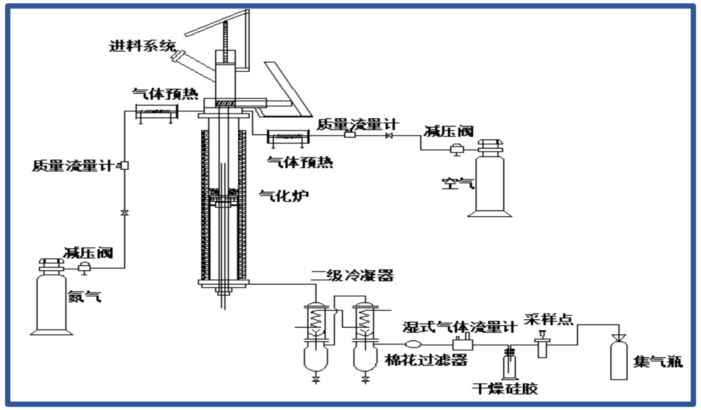
■ Materials and Equipment



Biogas residue was obtained from a AD base in Shandong
The AD tank capacity is 15m^3

Proximate analysis (wt%, ad)				Elemental analysis (wt%, ad)					LHV (MJ/ kg)
V	A	M	FC	C	H	O	N	S	
59.91	23.03	5.96	11.10	36.04	5.14	31.66	2.28	1.85	13.05

Fixed bed gasifier（600-800 ºC）



Fixed bed air GS test system

Fixed bed gasifier

1. electric heating
2. inner diameter: 51.5mm，height: 78.5cm

Fixed bed air GS test system

1. feed system
2. gas supply system
3. gasifier system
4. tar collection system
5. GS gas collection system

Waste Management (2017, 69, 162-9)

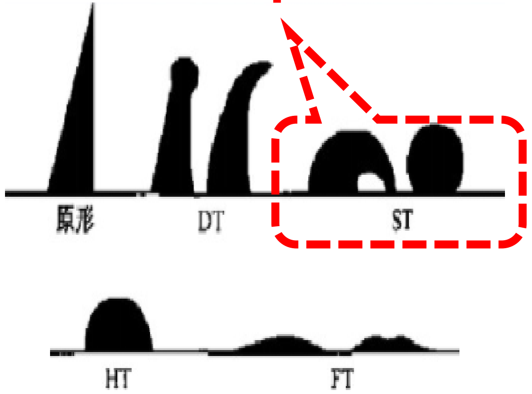
2.1 GS potential of biogas residue

■ Ash fusibility of biogas residue GS

Ash fusion point of biogas residue

Characteristic temperature(°C)	Abbreviation	Biogas residue	Pine with bark (Gilbe et al., 2008)
deformation temperature	D_T	1151	1350
softening temperature	S_T	1180	1370
hemisphere temperature	H_T	1208	1380
flow temperature	F_T	1335	1450

Ash fusion point



(a)800°C,ER=0.25

(b)800°C,ER=0.26

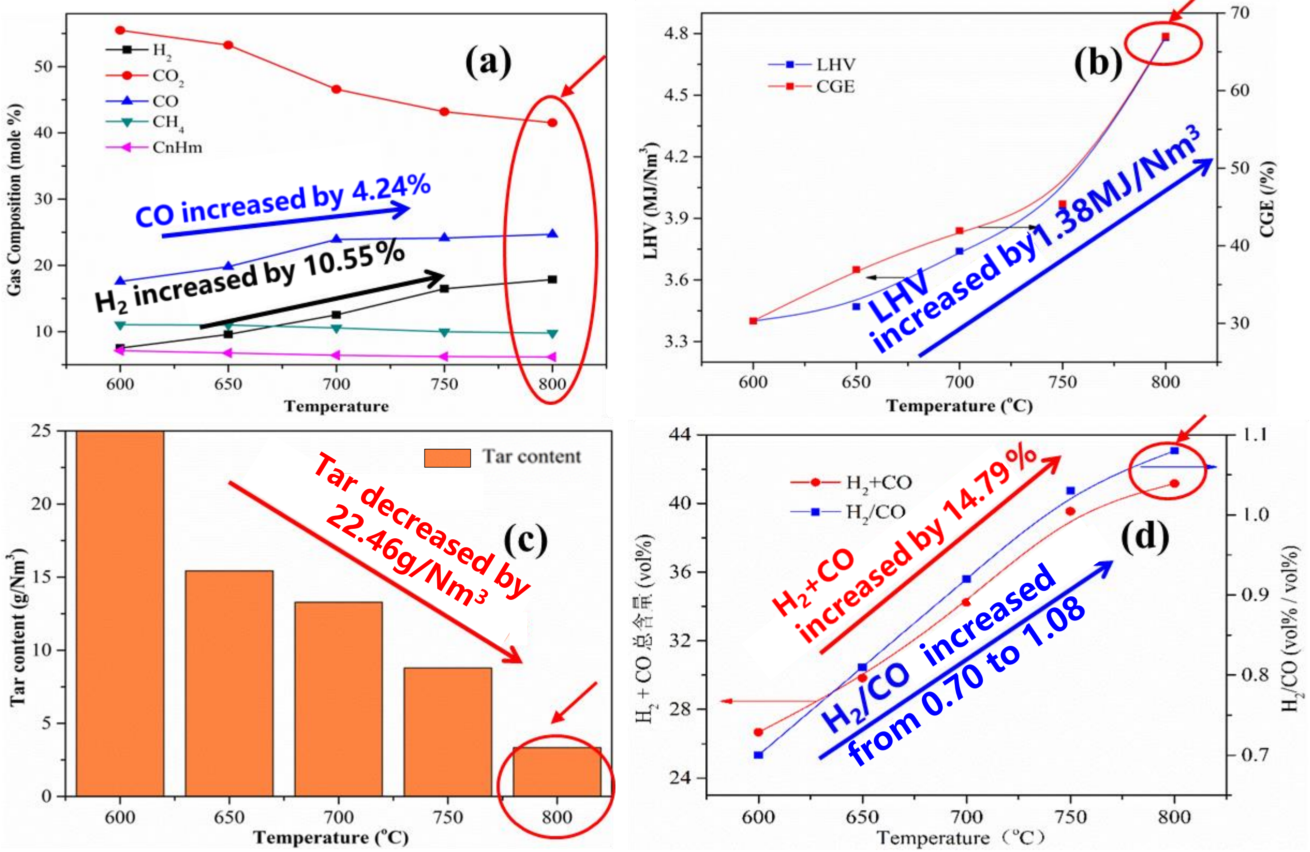
(c)800°C,ER=0.28

(d)800°C,ER=0.30

- Softening temperature（1180°C）of biogas residue is much higher than the maximum monitored temperature（1000°C） of oxidation section in gasifier chamber
- Biogas residue ash is soft, easy to pulverize; no slag is formed during air GS of at 600~800°C, then the process is feasible.

2.1 GS potential of biogas residue

■ Effect of GS temperature



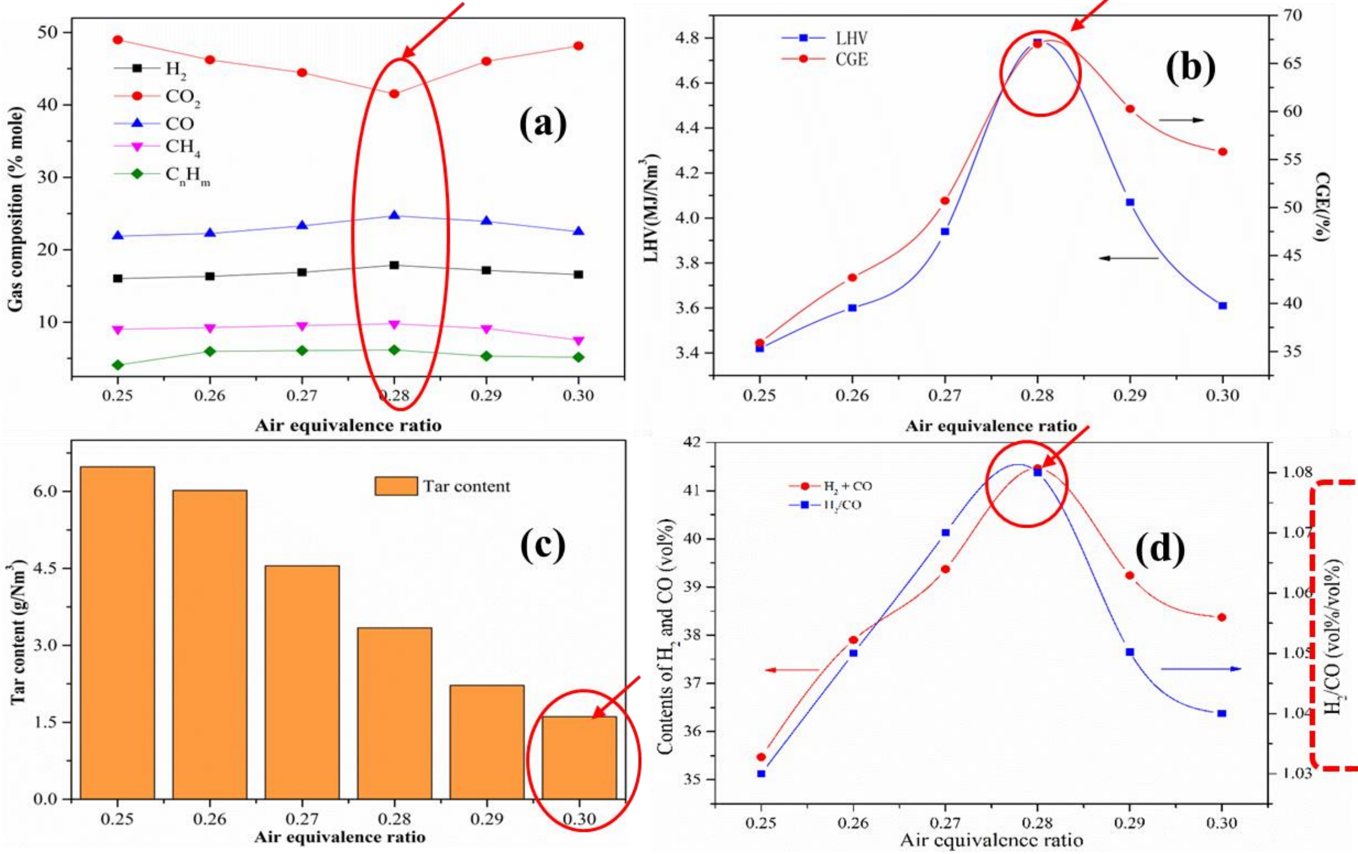
T=600-800℃

ER=0.28

- High temperature enhances endothermic reaction, promoting the formation of combustible components (H_2+CO)
- High temperature enhances tar cracking and reducing tar content
- GS effect is best at 800℃, LHV=4.78MJ/Nm^3 CGE=67.01% Tar=3.34g/Nm^3

2.1 GS potential of biogas residue

■ Effect of ER



T=800℃
ER=0.25-0.30

ER=0.28-0.30
LHV=4.78MJ/Nm³
CGE=67.01%
Tar=1.61g/Nm³

- H_2/CO>1
- H_2/CO=1-2, chemical synthesis
- Cellulose degradation and lignin enrichment improves the of H_2/CO (molar ratio) in biogas residue GS gas to some extent, which is significantly better than that of straw without AD

- The effect of ER on the GS characteristics of biogas residue is nonlinear. Appropriate ER is conducive to the formation of H2 and CO, and maintain a high LHV.
- Furthermore, the increase of bed temperature brought by the increase of ER was conducive to the secondary cracking of tar, Tar=1.61g/Nm³ (1/3 of conventional biomass)

2.1 GS potential of biogas residue

■ Physical and chemical properties of GS residue

Physical and chemical properties of GS residue of biogas residue

Char	Biogas residue GS	Switchgrass GS	Corn stover GS	Rice husk pyrolysis
BET surface area (m²/g)	**24.28**	**31.40**	**23.90**	**25.60**
M (wt. %)	2.70	2.50	1.90	0.00
VM (wt. %)	10.81	10.30	5.50	12.80
Ash (wt. %)	49.54	53.00	54.00	51.30
FC (wt. %)	36.95	34.30	38.50	36.00
C (wt. %)	44.08	42.80	38.50	45.20
H (wt. %)	3.47	1.60	1.30	1.50
N (wt. %)	3.10	0.80	0.70	0.40
S (wt. %)	0.00	0.17	0.09	0.00
HHV (MJ/kg)	**16.84**	**15.86**	**15.29**	**14.40**

Comparison of inorganic components and heavy metals content of biogas residue GS ash with Chinese organic fertilizer standard（NY 525-2012，2012)

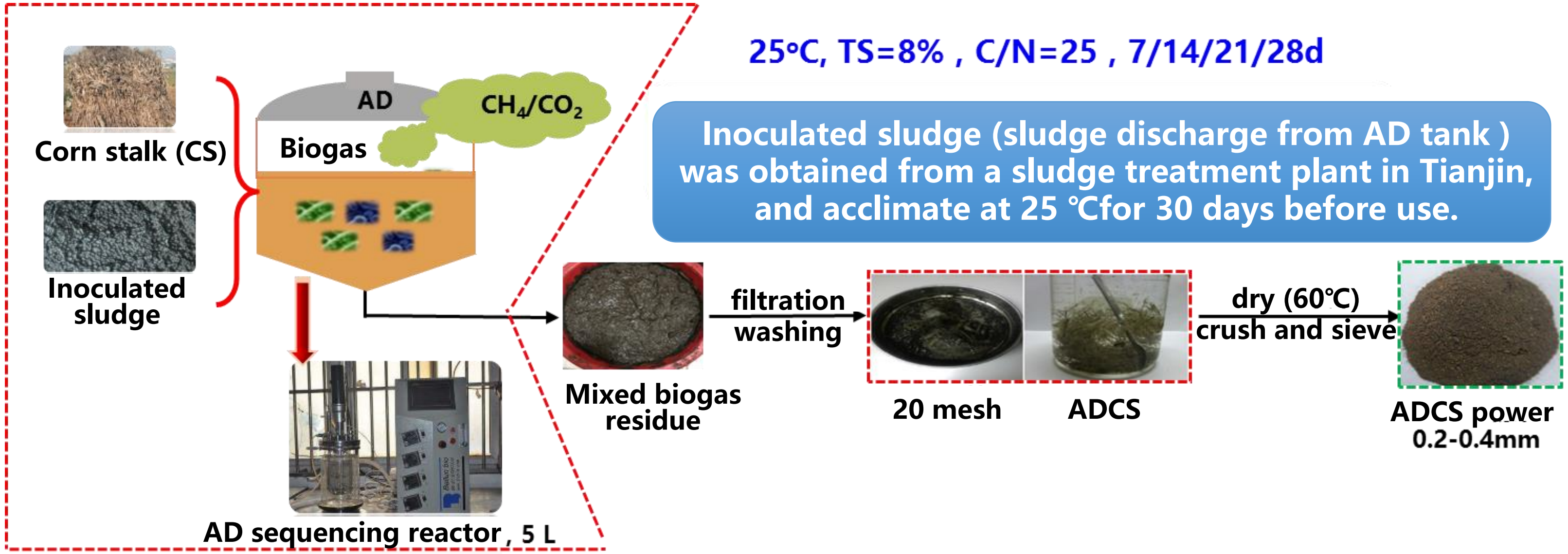
Element	P_2O_5	SiO_2	CaO	MgO	Fe_2O_3	K_2O	Al_2O_3	SO_2	Na_2O	TiO_2
Content/%	26.96	24.11	19.85	8.45	5.17	4.29	3.09	3.08	0.57	0.49

Element (ppm)	Cd	Cr	As	Pb	Hg
Detection value	1.22	296.48	6.45	19.96	n.d.
Thresholds for organic fertilizer standard	3	150	15	50	2

- **GS residue:** limited specific surface area（24.28m²/g），a large content of inorganic components（49.54%）. Not suitable for carbon adsorption material or activated carbon precursor, but suitable for **soil organic fertilizer.**
- **GS residue is rich in P**：Slow release、Match the growth rate of crop、Reduce the risk of eutrophication

2.2 Effects of AD on GS

■ Design and results of AD pretreatment experiments



Experimental program

- ✓ Sample preparation with different AD times (7-28d)
- ✓ Collection of AD pre-treated CS
- ✓ Preparation ADCS powder for GS

Elemental analysis, proximate analysis, H/C and Heating value analysis of CS and ADCS

Item	CS	ADCS-7d	ADCS-14d	ADCS-21d	ADCS-28d
C (wt%)	42.51	44.38	44.47	42.30	43.03
H (wt%)	5.89	5.79	5.78	5.50	5.59
O [a] (wt%)	41.19	39.04	39.57	40.30	38.68
N (wt%)	2.35	2.00	1.97	1.85	1.66
H/C (molar ratio)	1.66	1.57	1.56	1.56	1.56
V(wt%)	72.81	67.66	66.99	63.94	63.08
M (wt%)	8.06	8.79	9.21	9.24	9.75
FC (wt%)	12.91	17.60	18.41	21.4	21.12
LHV (MJ/kg)	14.64	15.53	15.62	14.20	14.76

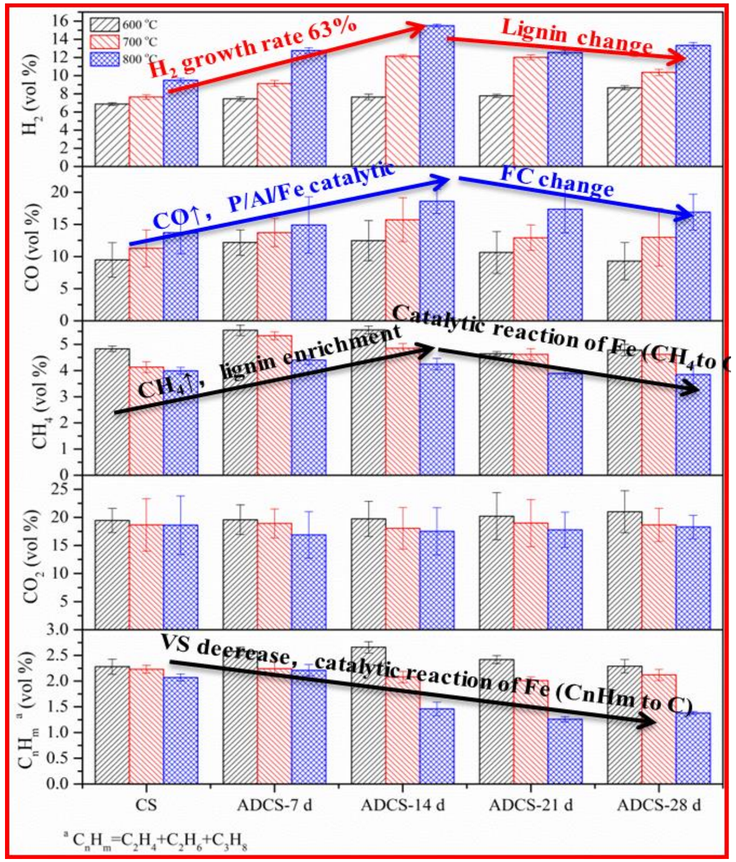
ADCS

1. C↑, O↓
2. H/C↓, aromaticity↑
   (Enrichment of lignin)
3. FC↑, LHV↑
4. ADCS-14d: inflection point
5. Change of 1-3 is helpful to improve the pyrolysis and GS characteristics

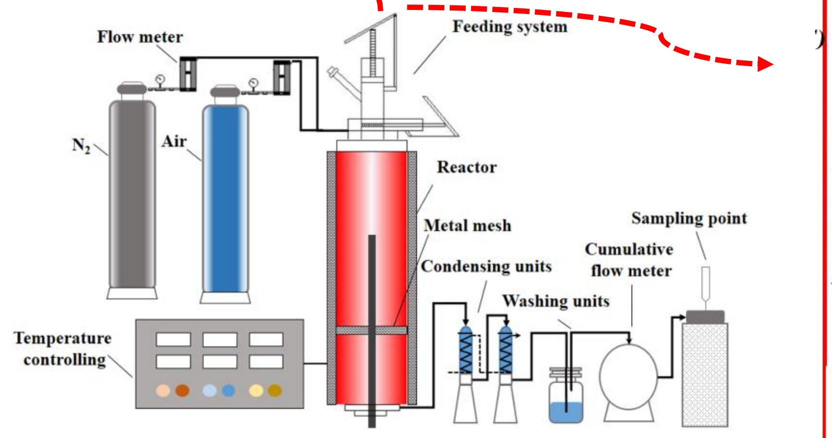
Fuel.(2019; 324-333)

2.2 Effects of AD on GS

■ GS characteristics of CS and ADCS

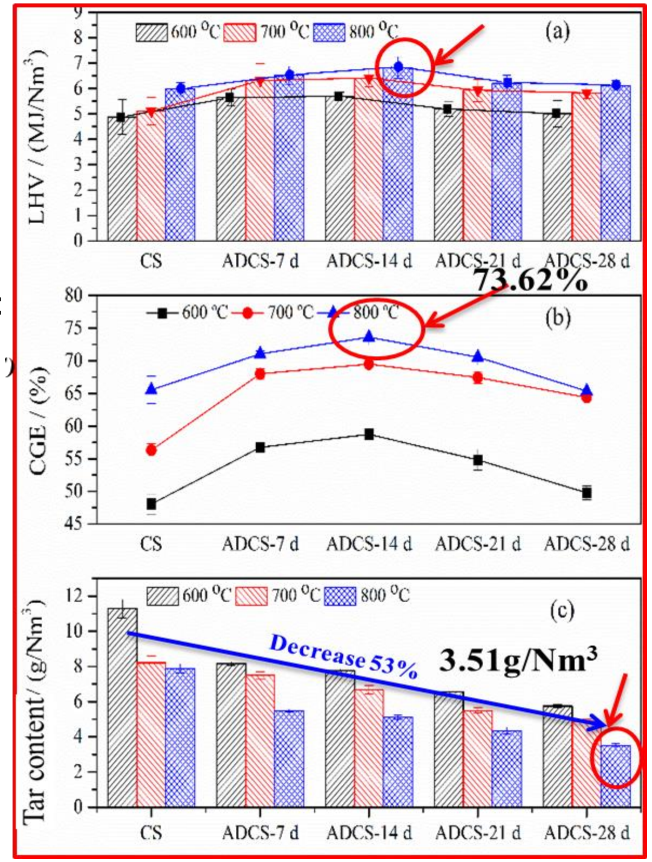


Gas composition of samples (CS, ADCS-7 d, ADCS-14 d, ADCS-21 d and ADCS-28 d).



Schematic of gasification experimental procedure.

Gasification performance of CS and ADCS (a) LHV, (b) CGE and (c) Tar content



- Gasification of ADCS-14d resulted in the highest H_2 content (15.50 vol%) at 800 °C and increased about 63 vol% compared with the untreated CS (9.5 vol %).

- ADCS-14d has the optimal of gas production and CGE (73.62%) at 800 °C, and shorter retention time between 7d to 14d was recommended with superior values than the longer retention time.

2.2 Effects of AD on GS

■ Physical properties of CS and ADCS

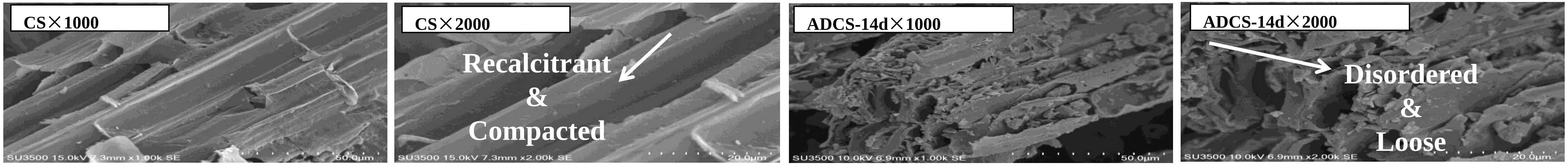
Inorganic element composition of CD and ADCS (ppm)

Element	CS	ADCS-7d	ADCS-14d	ADCS-21d	ADCS-28d
Na	299.00	260.86	211.83	226.23	180.85
Mg	2108.50	1619.12	1674.38	1591.13	1638.00
P	1879.23	2889.93	3088.33	3344.49	3426.92
K	19736.54	1692.17	1704.24	1510.45	1723.26
Ca	10765.86	12506.91	13229.51	12665.40	13051.07
Fe	1122.76	9961.71	11250.02	12638.47	12926.55
Al	763.80	1973.10	2213.65	2504.58	2699.60

BET specific surface area, pore volume and aperture of CS and ADCS

Sample	BET specific surface area (m^2/g)	pore volume (cm^3/g)	aperture(nm)
CS	0.1052	0.009877	187.8
ADCS-7 d	1.05	0.01293	24.61
ADCS-14 d	2.893	0.01791	12.38
ADCS-21 d	3.051	0.01961	12.85
ADCS-28 d	1.868	0.01855	19.86

- Significant enrichment of P、Fe、Al, catalyzing the formation and release of CO and CH_4 (reinforce WGS).
- Specific surface area of ADCS improved significantly, decreased slightly after 21d, which may be due to the excessive decomposition of AD microorganisms, so that CS structure partially collapsed.
- Fiber structure of CS is orderly and compact, while of ADCS is disorderly and loose.
- The improvement of porosity could enhance the contact and reaction of reactants during GS, thus improving the GS performance of ADCS.

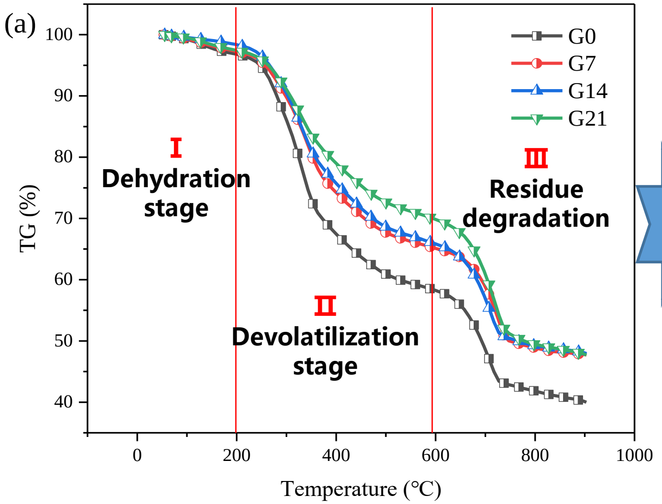


SEM images of CS and ADCS

2.2 Effects of AD on GS

■ Thermogravimetric characteristics and volatile emission

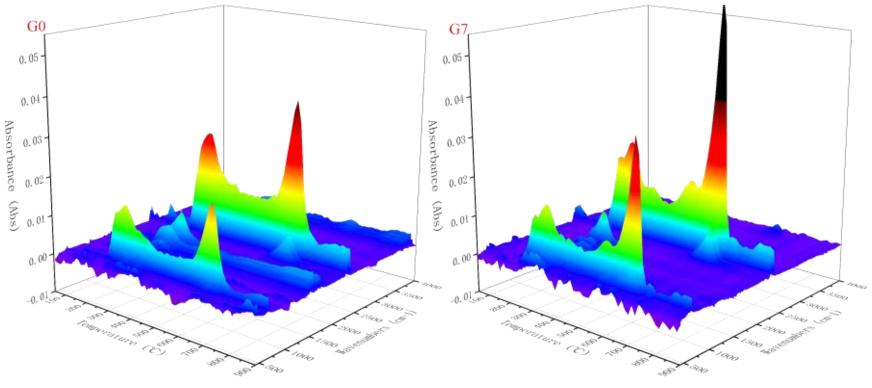
TG analysis

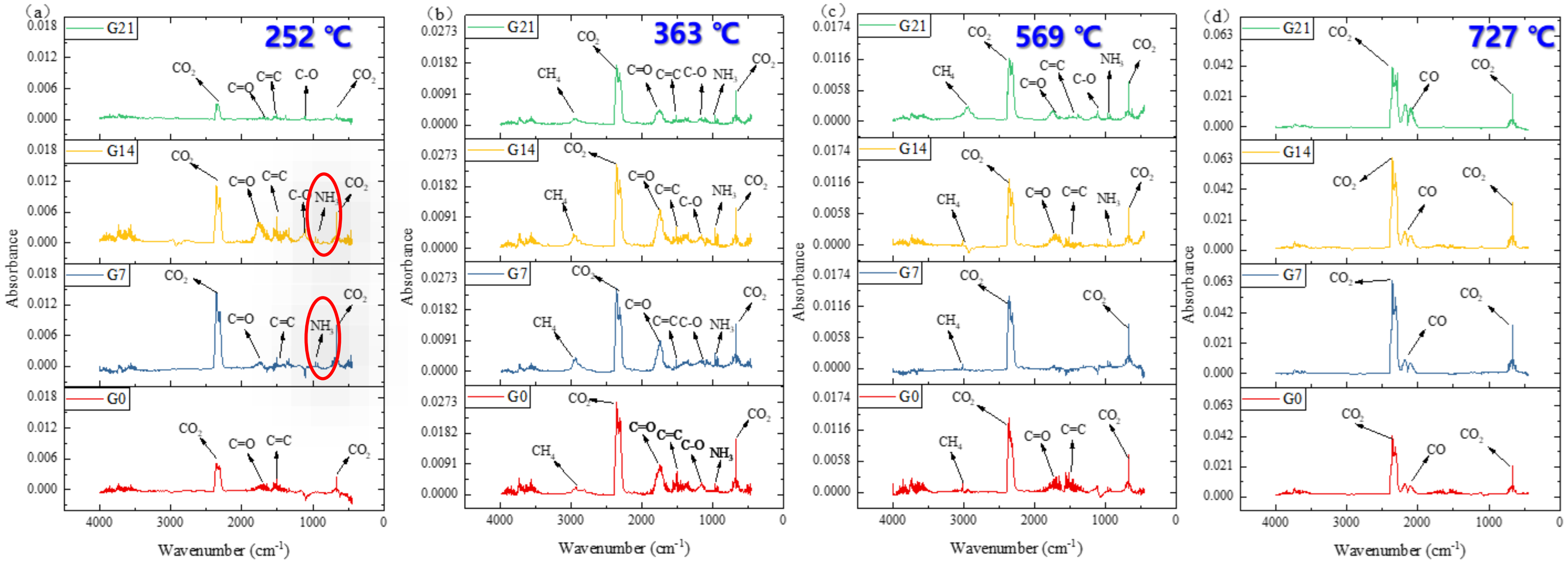


Select typical temperatures

1. Initial degradation	252 ℃
2. Max degradation rate (Ⅱ)	363 ℃
3. End of devolatilization stage	569 ℃
4. Max degradation rate (Ⅲ)	727 ℃

Online FTIR profiles of raw materials at typical TG temperatures





- Moderate AD has a **depolymerization effect** on raw materials, which is beneficial to the preferential release of some functional groups and gases
- Excessive AD **increases the thermal stability** of raw materials and reduces the release intensity of products

Bioresource Technology.(2022; 126496)

2.2 Effects of AD on GS

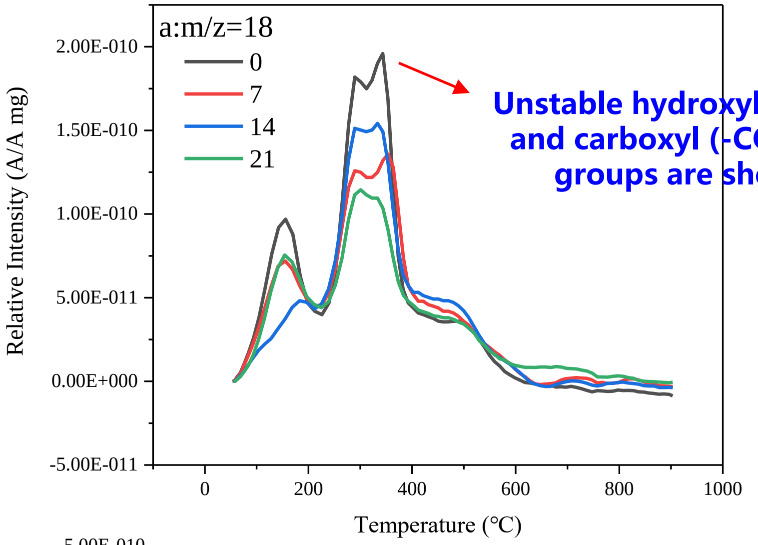
■ Evolution of functional groups

1. Char self-GS and tar secondary cracking

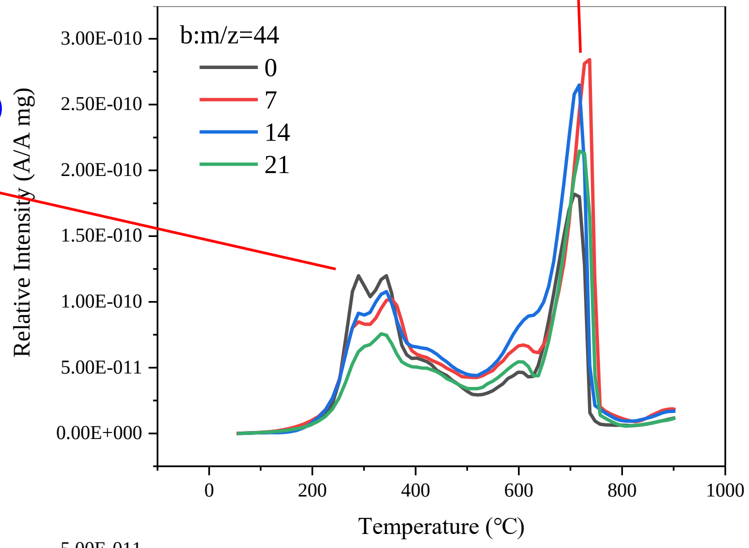
$C+H_2O \leftrightarrow CO_2+H_2$

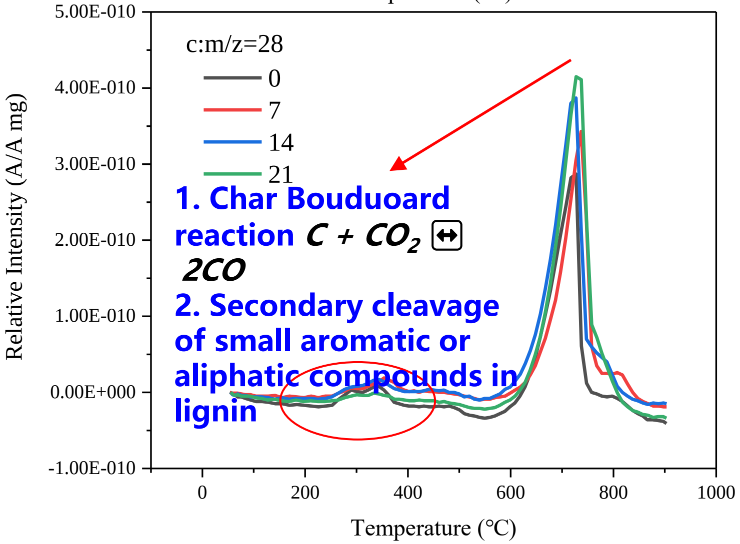
$C_nH_mO_p+(2n-p)\ H_2O \leftrightarrow nCO_2+(1/2m+2n-p)H_2$

2. Inorganic salts decompose at high temperature



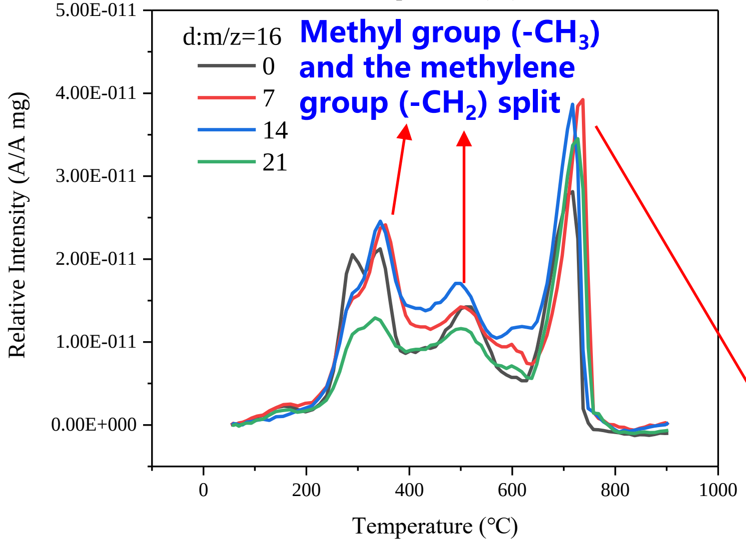
Unstable hydroxyl (-OH) and carboxyl (-COOH) groups are shed





1. Char Bouduoard reaction $C + CO_2 \leftrightarrow 2CO$

2. Secondary cleavage of small aromatic or aliphatic compounds in lignin



Methyl group ($-CH_3$) and the methylene group ($-CH_2$) split

Deformation and cracking of aromatic ring and degradation of Methoxy Group ($-O-CH_3$)

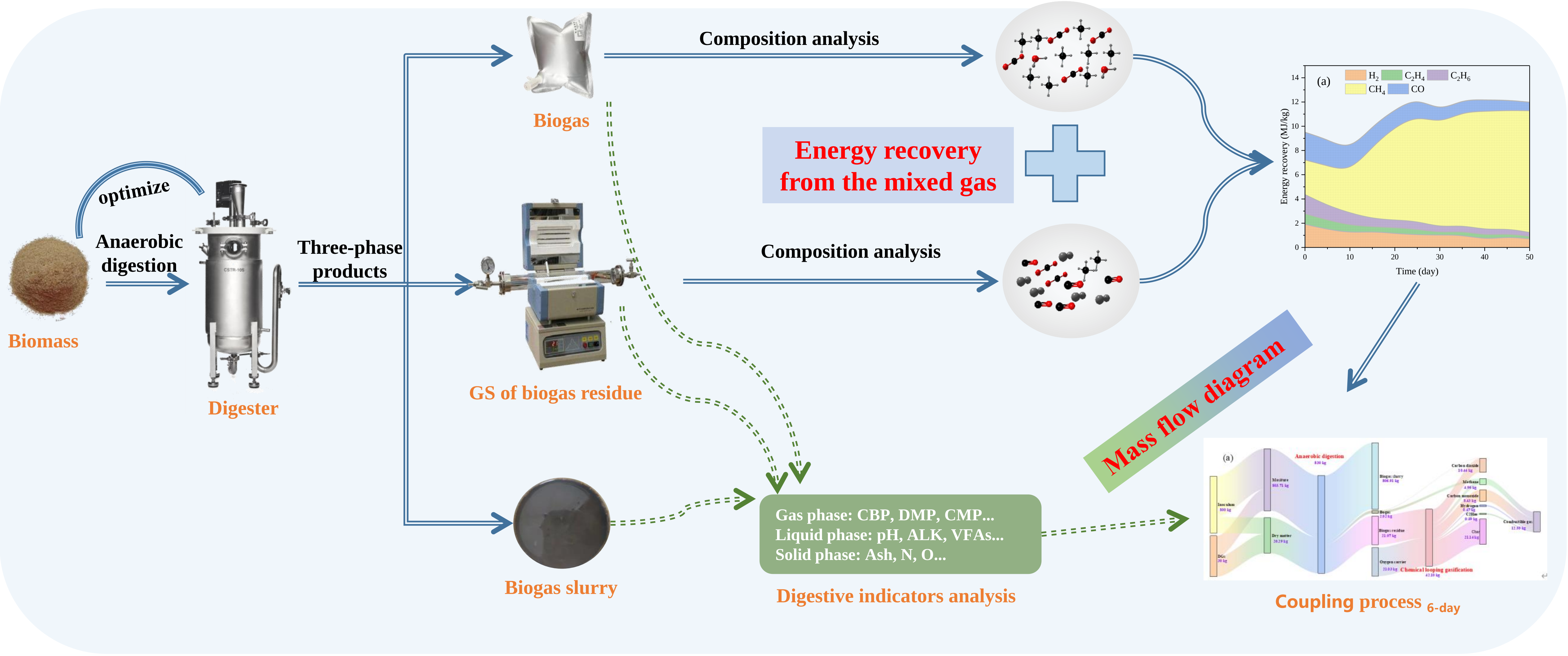
- The combination of raw material characterization and online-FTIR showed that moderate AD had a **positive effect** on gas release.
- MS analysis showed that AD affected the gas release, mainly in two aspects:

(1) AD at low temperature **changes the release intensity of some functional groups**, and then affects the corresponding gas release

(2) Moderate AD at high temperature is beneficial to char degradation and tar secondary cracking, and to improve the intensity of CO and CO_2 release

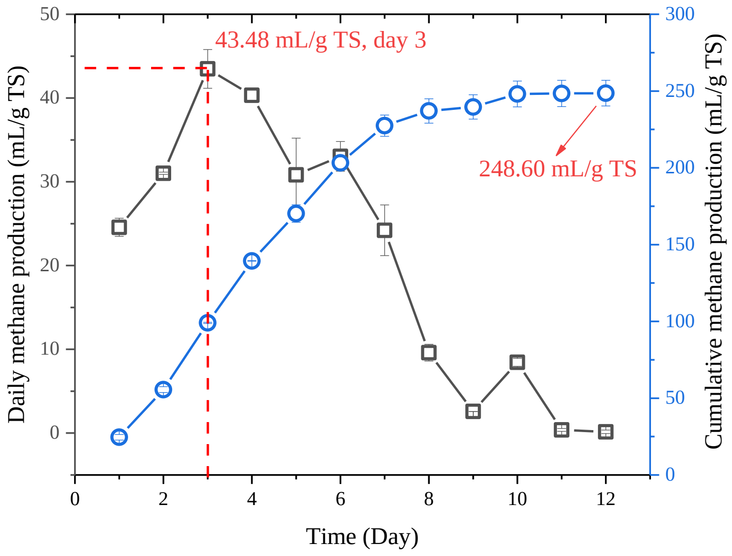
2.3 Novel process as controllable AD-GS

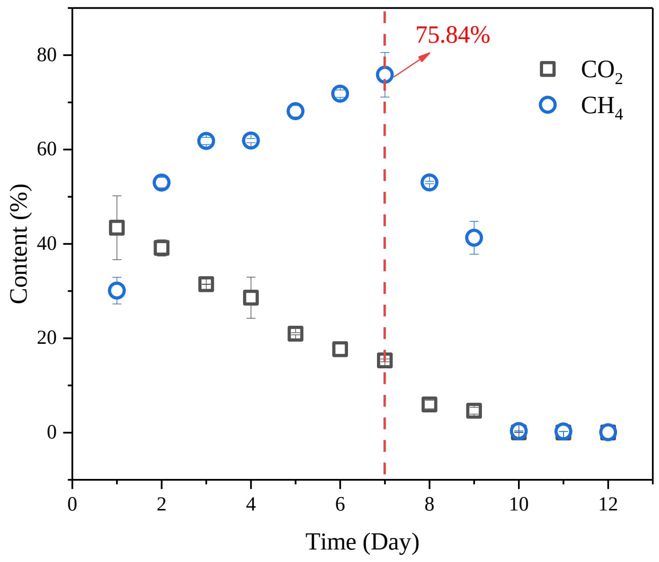
■ Experimental procedures and results



2.3 Novel process as controllable AD-GS

■ Biogas production and solid degradation in AD



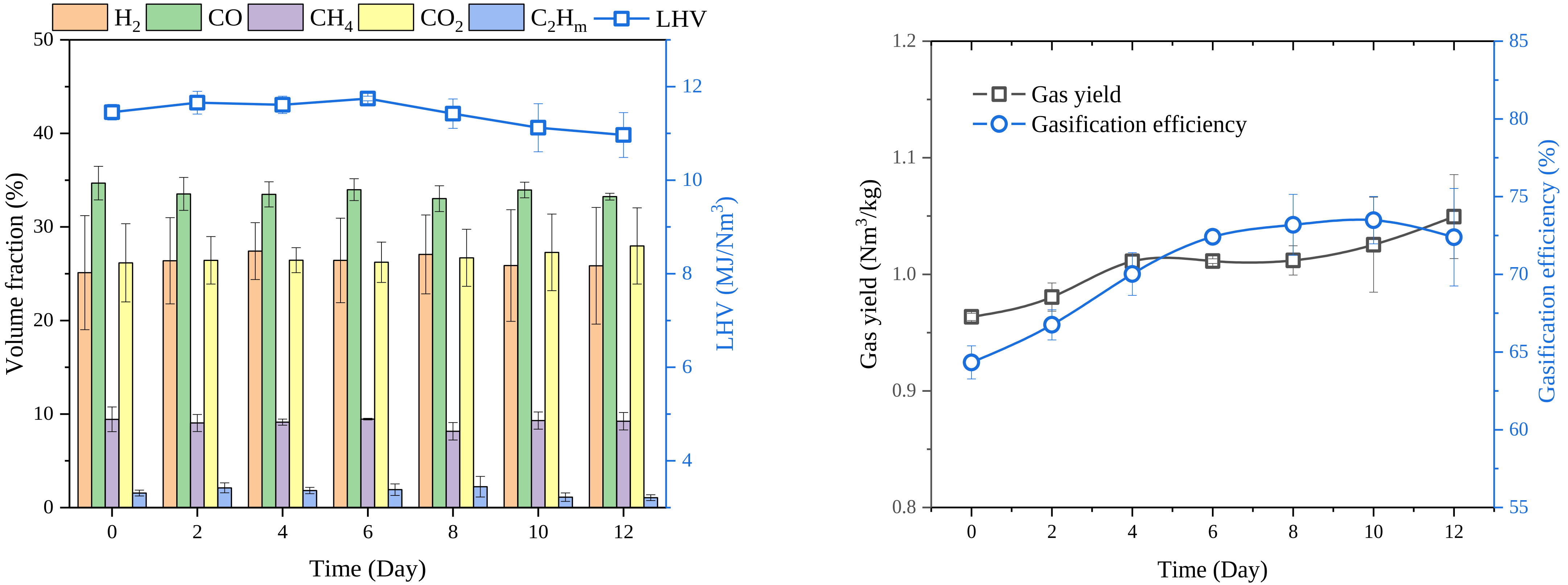


- **Biodegradable components (Hem and Cel) were rapidly consumed and converted to methane in initial AD;**
- **The solid degradation of anaerobic digestion was only 29.06%, and the non biodegradable lignin was enriched.**

Parameters	Anaerobic digestion intensity (day)						
	0	2	4	6	8	10	12
Solid residues (g)	26.29±0.92	24.86±0.46	22.85±0.01	21.07±0.44	19.00±1.71	18.68±0.14	18.65±0.24
Ash (wt.%)	15.87	18.15	20.69	23.07	24.67	24.26	24.73
Hemicellulose (wt.%)	5.52±0.10	5.65±0.81	6.04±0.03	6.25±0.20	6.46±0.20	6.53±0.17	6.39±0.35
Cellulose (wt.%)	25.93±0.59	20.11±1.19	13.67±0.54	11.27±0.34	11.50±0.26	11.27±0.33	11.21±0.80
Lignin (wt.%)	38.56±0.87	39.72±0.86	40.03±1.53	44.14±1.12	42.69±2.72	42.49±1.56	42.39±0.18
Solid degradability (%)	-	5.45	13.07	19.86	27.75	28.94	29.06
Hem degradability (%)	-	3.29	4.84	9.32	15.47	15.96	17.87
Cellulose degradability (%)	-	26.67	54.17	65.16	67.96	69.10	69.33
Lignin degradability (%)	-	2.59	9.75	8.26	20.00	21.70	22.00
Lignocellulose degradability (%)	-	11.57	25.81	29.42	37.40	38.80	39.21

2.3 Novel process as controllable AD-GS

■ GS performance of biomass with different AD intensities

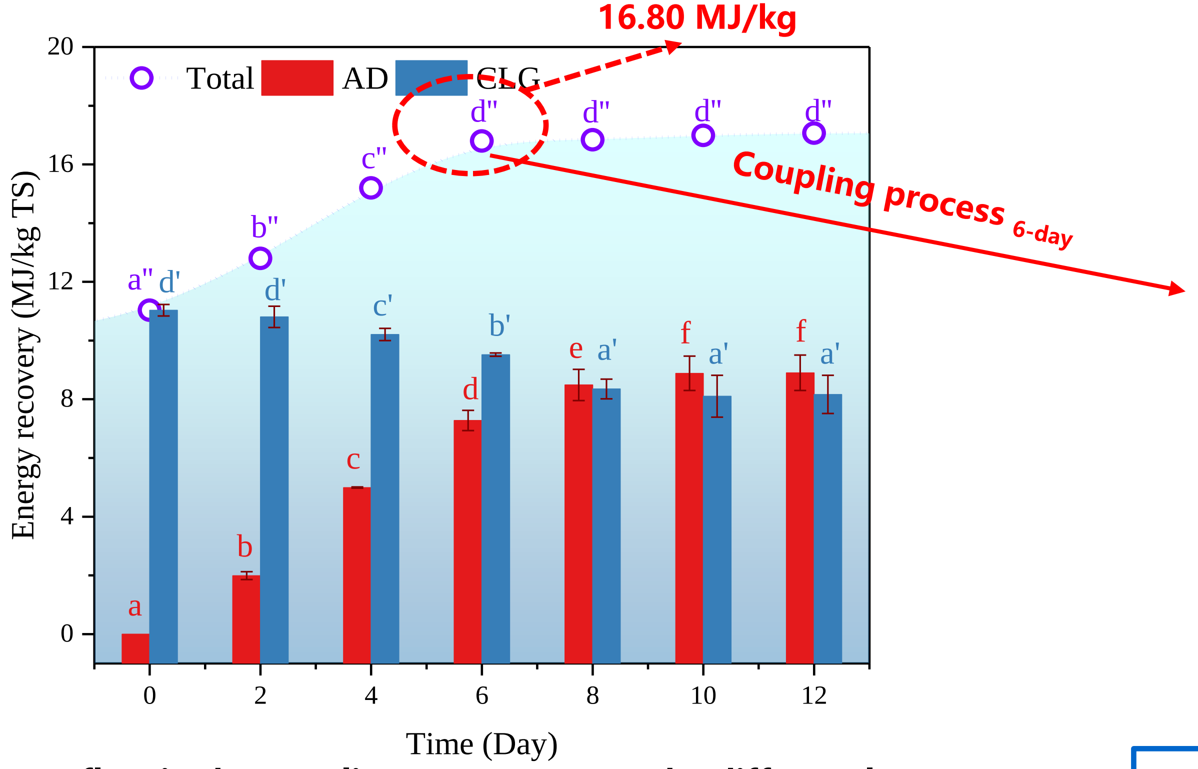


GS performance. (a) Volume fraction of syngas; (b) Gas yield and gasification efficiency

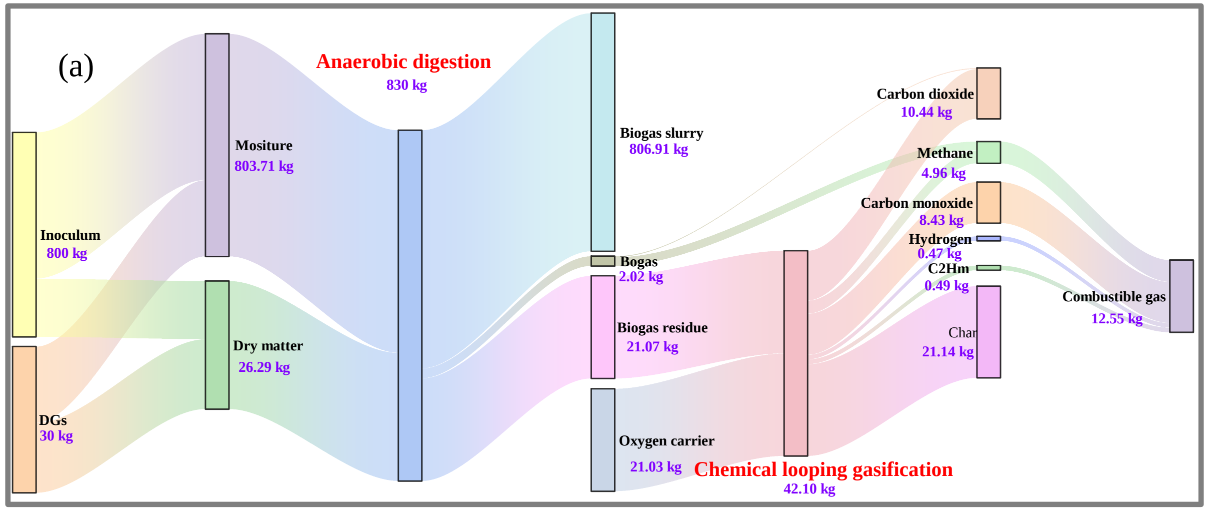
- **Gasification efficiency was significantly improved with the mild AD intensity, and 72.41% of the gasification efficiency was obtained in biogas residue on day 8 of AD.**
- **Part of the excess consumption of organic matter through longer AD posed a negative influence on LHV of syngas produced by GS, leading to a decrease in gasification efficiency.**

2.3 Novel process as controllable AD-GS

■ Effect of AD intensity on mass and energy balance



Energy flow in the coupling process. Note: the different letters denoted significant difference (P<0.05), while the same letters showed not significant difference (P>0.05).



Mass distribution in novel gasification process (6-day AD)

- The energy recovery of AD **increased significantly** from the beginning to day 10 (P<0.05) and then **leveled off to** day 12.
- While that of GS presented **a downward trend** due to the **energy competition** between AD and GS.

- The energy recovery of 6-day AD-GS could reach **16.80 MJ/kg**, which was only 1.60% lower than that of 12-day AD-GS.
- In the case of coupling process $_{6\text{-day}}$, relatively **higher energy recovery** (16.80 MJ/kg TS), **mass conversion** (47.73%) and **carbon efficiency** (55.06%), and **relatively lower CO_2 emissions** (39.72%) were achieved in a **shorter process cycle**.

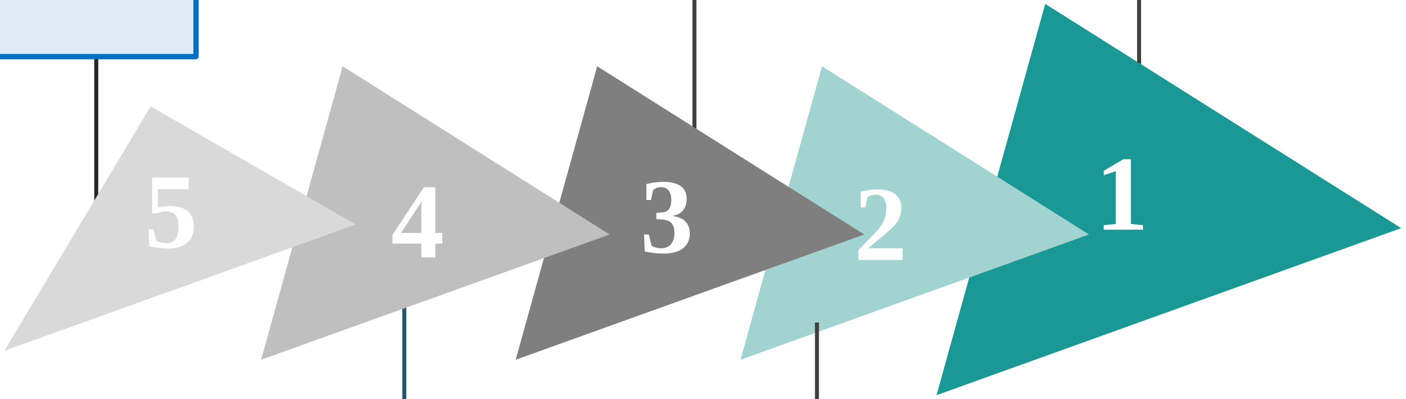

3 Future perspectives

3.1 Obstacles to novel gasification

Tuning the GS process to obtain a more suitable char for the scope, eventually sacrificing a share of the cold gas efficiency, may play a key role in the future

Novel gasification with bio-thermochemical coupling technology is still in the exploratory stage

The lack of engineering cases for the novel gasification concept necessitates its feasibility to be verified



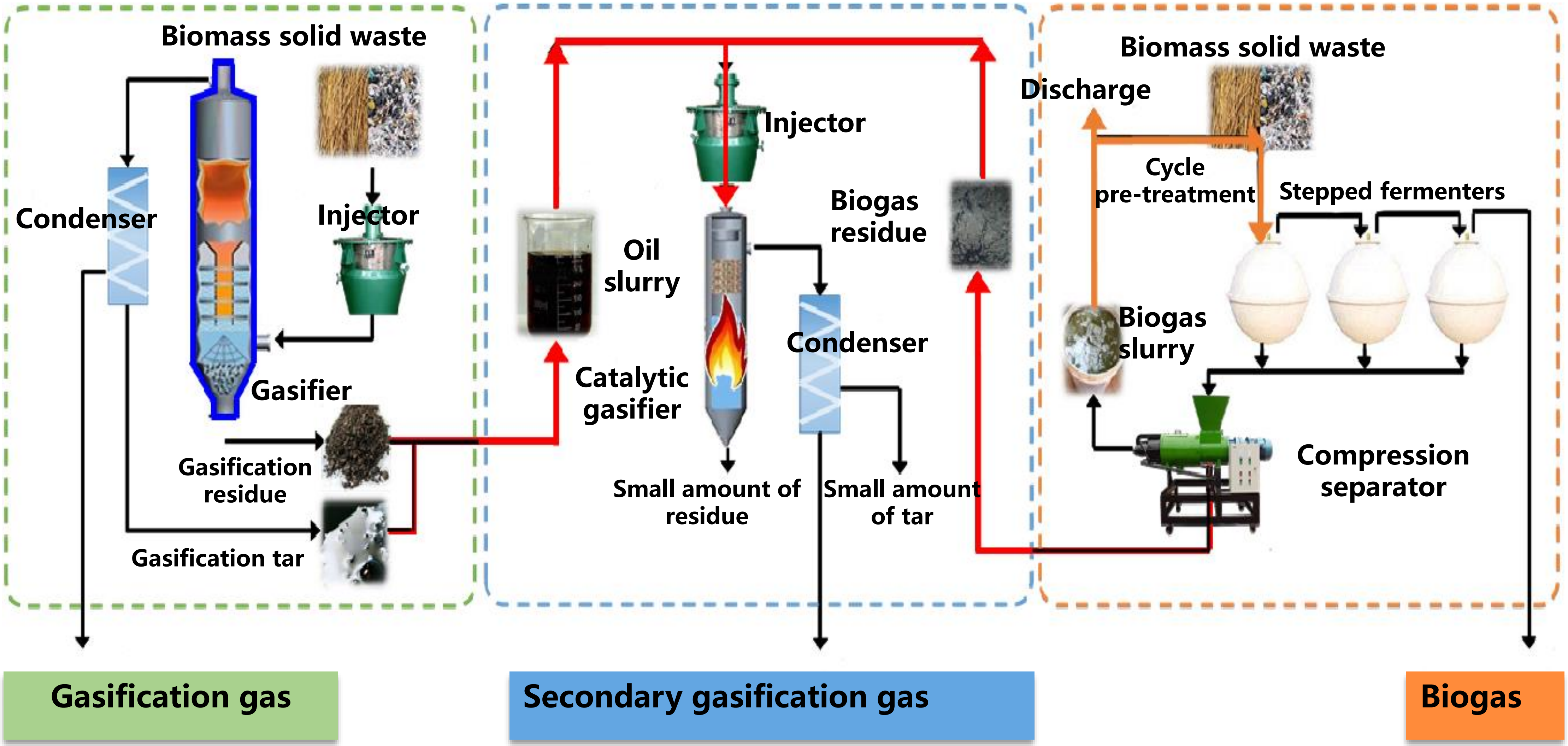
The main limit is the GS temperature that had to be kept below 800 °C by the risk of ash melting. This limited the syngas heating value to 5.3 MJ m^{-3} and the efficiency to 70%;

A strongly energy intensive pre-drying phase has to be taken into account for the biogas residue, making this route even more challenging


4 Gasification in TJU and TJCU

Gasification in TJU and TJCU

New-type clean gasification for multiple biowaste



Gasification in TJU and TJCU

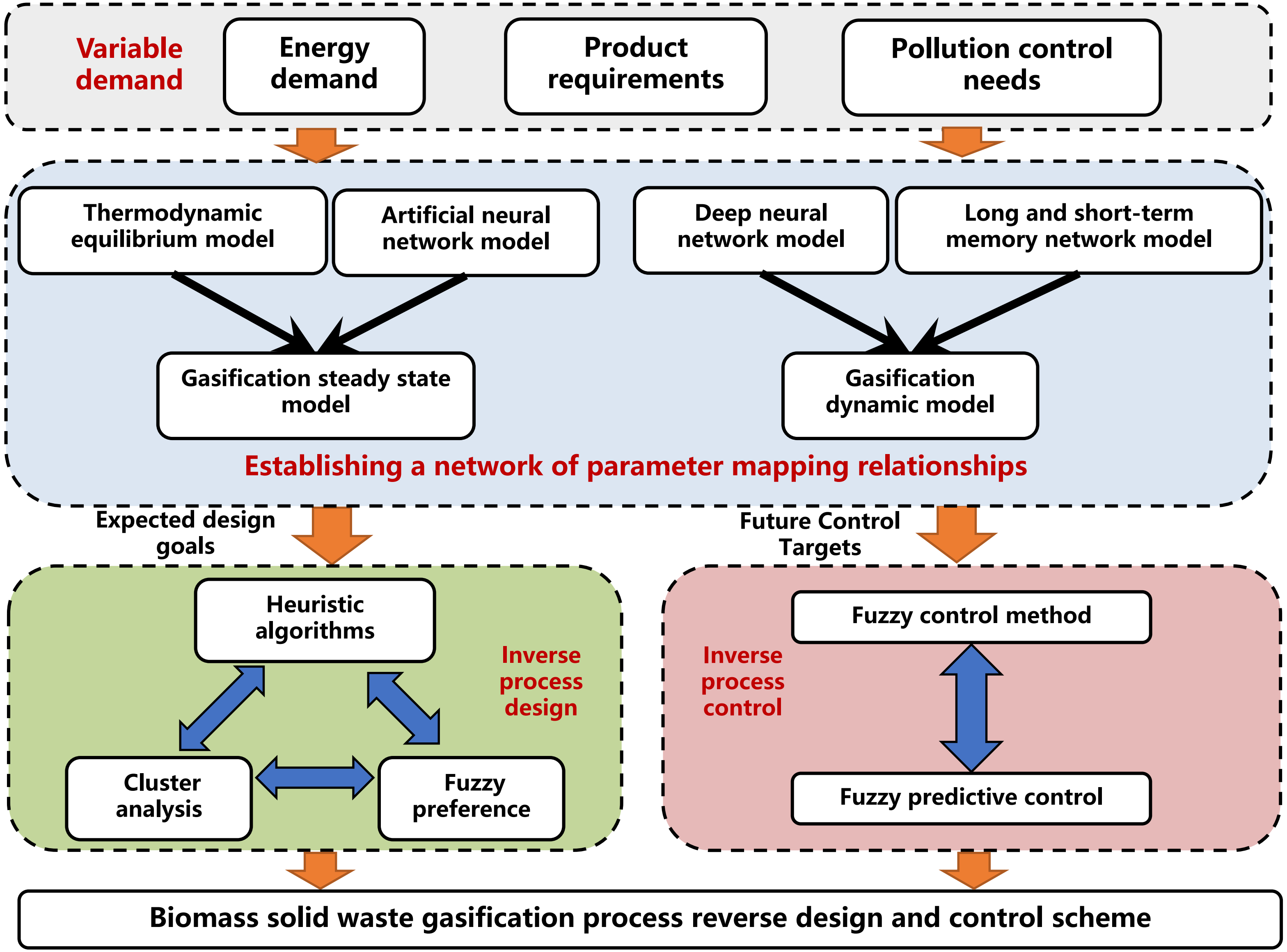
Innovative design of gasification: Reverse design

Reverse design method flow

Step1.
Define user needs

Step2.
Combining theoretical derivation and empirical modeling to construct a network of parameter mapping relations

Step3.
Heuristic algorithm combined with fuzzy control theory to form optimal solutions



Research teams

Guanyi Chen **vice president and professor of Tianjin University of Commerce**

- **Distinguished professors of Changjiang Scholars, leading talents of the 10000 person plan, and leading talents of ecological and environmental protection**
- **National outstanding scientific and technological workers enjoy the special government allowance of the State Council**
- **Baosteel excellent teachers and the first batch of Tianjin outstanding talents**

He is mainly engaged in research on **biomass waste energy conversion**. He presided over key projects of the National Natural Science Foundation, projects/topics of the Ministry of science and technology, EU projects, etc. Now he is a member of the overall expert group of the key special project of the national key R & D plan "technological innovation in green livable villages and towns", the convener of the biomass gas environment and safety group of TC 255 Committee of ISO international organization for standardization, the director of Tianjin Key Laboratory of biomass waste utilization, and the president of Tianjin Institute of sustainable development.

Beibei Yan **Professor of Tianjin University**

- **Winner of National Science Fund for Outstanding Young Scholars**
- **Winner of Tianjin Youth Science and Technology Award and Tianjin outstanding youth fund**
- **Young leading talents and young scientific and technological talents in Tianjin**
- **Secretary of the Council of national solid waste energy industry technology innovation strategic alliance**

Research teams


Members of Tianjin University


Yingjin Song
associate professor


Zhanjun Cheng
associate professor


Fawei Lin
associate professor


Ning Li
associate professor


Xiaoqiang Cui
associate professor

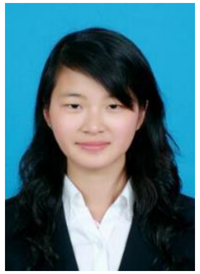

Jian Li
postdoctor


Shengquan Zhou
postdoctor

Member of Tianjin University of Commerce


Junyu Tao
lecturer


Yunan Sun
lecturer


Lan Mu
lecturer


Xiaohua Wang
Experimentalist


Hong Su
Experimentalist


Biyu Wang
Experimentalist

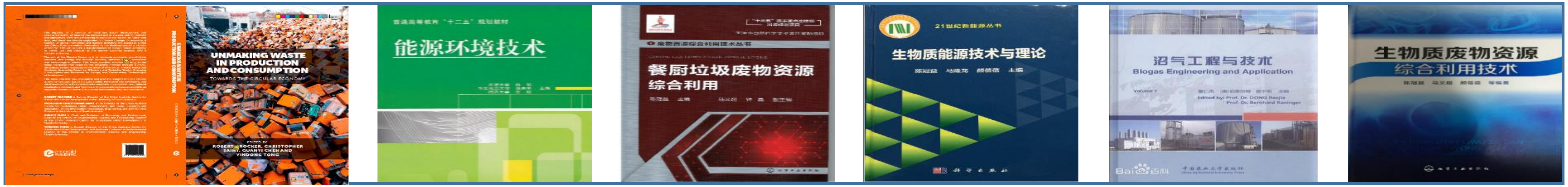
Member of Tibet University


Xuebin Lv
professor


Zeng Dan
associate professor

Achievements

Academic achievement: more than 450 papers; 41 patents (including Japan, USA, Australia patents); 6 software registrations; 1 international standard and 9 books.



Acknowledgements:

1) Ministry of Science and Technology of the People's Republic of China
2) National Natural Science Foundation of China
3) Tianjin Municipal Science and Technology Bureau
4) Tianjin university, Tianjin University of Commerce
5) All team members
6) IEA Bioenergy

Thanks for your attention！

谢谢！

Email: yanbeibei@tju.edu.cn
Tel.： +86-22-87402075/87402100