POLITECNICO DI TORINO

Corso di Laurea in Ingegneria Chimica e dei Processi Sostenibili

Tesi di Laurea Magistrale

Catalytic pyrolysis of biomass

Effect of different bed materials for biomass pyrolysis in a thermogravimetric fluidized bed reactor

Relatore
prof.ssa Tonia Tommasi

Correlatore:
prof. Daniel Serrano Garcia

Alice Alleati
matricola: 243754

Ottobre 2019

A mia nonna Lucia

Summary

Introduzione

Negli ultimi decenni, il tema dello smaltimento dei fanghi prodotti dagli impianti di depurazione (SS) delle acque di scarico urbane, è diventando sempre più urgente.
A questo proposito, svariati gruppi di ricerca si sono proposti di trovare una strategia percorribile per risolvere tale problematica.
Una delle proposte che attualmente sembra essere la più accreditata è quella di sottoporre il SS a pirolisi, ottenendone la stabilizzazione, il dimezzamento del volume e l'intrappolamento dei metalli pesanti, in esso presenti.

Dalla pirolisi, sono originati tre prodotti: il bio-olio (liquido), potenzialmente trasformabile in biocombistibile, il bio-char, utilizzabile come carbone attivo per il sequestro della CO_2 o per la rimozione di inquinanti e una frazione gassosa, sfruttabile per autosostenere il consumo energetico richiesto dal processo stesso o per la produzione di syngas.

Tuttavia, ancora sono presenti diversi ostacoli di tipo tecnico ed economico, ad impedirne la diffusione su grande scala, tra i quali spiccano l'elevato costo del bio-olio prodotto, la mancanza di un'adeguata campagna di standardizzazione e caratterizzazione del biocombustibile, la sua non completa compatibilità con gli attuali carburanti derivanti dal petrolio e la scarsità di studi volti all'ottimizzazione del processo e al suo scale-up.

Il lavoro di ricerca da me svolto, si propone come obiettivo lo studio degli effetti causati dall'utilizzo di diversi materiali come letto fluidizzato in un reattore termogravimetrico, nel quale viene condotta la pirolisi di due diversi tipi di biomasse (SS e pellets in legno). I parametri di processo (temperatura, portata del gas inerte fluidizzante (N_2) e grandezza delle particelle di biomassa) sono stati fissati, adottando quelli selezionati da un precedente studio di ottimizzazione condotto dall'"Energy Systems Engineering Group" [16] dell'Università spagnola Carlos III.

Quello che si vuole valutare è la possibilità di utilizzare uno di questi minerali, per un'operazione di upgrading in-situ, per raggiungere un'efficienze maggiori di processo e produrre un bio-oil di qualità superiore.

I materiali selezionati sono la dolomite, l'allumina, la sepiolite e l'olivina. Sono minerali largamenti presenti in natura, già presi in considerazione da altre ricerche precedenti, sia per studi sulla pirolisi che sulla gassificazione. Tuttavia, i risultati trovati in letteratura sono spesso discordanti, o non confrontabili tra loro, in quanto i vari esperimenti sono stati condotti in condizioni di temperatura e di portata del gas fluidizzante differenti, con varie tipologie di biomasse e di reattori.

Materiali

Biomassa

Dipendentemente dal tipo di biomassa, si possono ottenere risultati molto diversi tra loro ed è, infatti, uno dei parametri che maggiormente influisce sui processi di pirolisi, essendo correlata non solo alla resa della reazione, ma anche alla qualità dei suoi prodotti.
Numerose sono state fino ad ora le ricerche volte all'individuazione della biomassa che meglio si presta a questi tipi di processi termochimici.
I parametri che sono stati selezionati come quelli maggiormente influenti sono principalmente tre:

- la percentuale di lignite, cellulosa ed emicellulosa di cui si compone la biomassa, è un fattore capace di dare indicazioni sulle possibili rese di char, bio-oil e syngas;
- il rapporto atomico O/C e H/C, permette la collocazione della biomassa in questione sul diagramma di van Kreveler, Figura 2.1 e fornisce un'indicazione sull'età geologica della stessa;
- la distinzione delle frazioni di umidità, volatili, fixed carbon e inerti.

Oltre al SS, Figura 2.4, è utilizzato anche del pellets, denominato "pellets asturias", appartenente alla categoria EN plus A1, ottenuto esclusivamente dal legno, Figura 2.2, presentante le caratteristiche tipicamente più idonee per l'ottenimento di alte rese di liquido. Questa scelta è stata fatta per avere un termine di paragone valido.

Le due biomasse, sono preliminarmente sottoposte ad una serie di analisi volte alla loro caratterizzazione, in modo da poter discutere sui risultati, consapevoli delle loro proprietà fisiche e chimiche.
In Tabella 1, sono riassunti i valori ottenuti dalla Proximate Analysis (TGA) e Ultimate Analysis (CHNO).
Dalla calorimetria il PCS è risultato 18,88 MJ/kg per il pellets e 13,77 MJ/kg per il SS.

Il wood pellets viene triturato, per ottenere una dimensione delle particelle confrontabile con quella dei fanghi, ed entrambe le biomasse sono setacciate nel range 1-2,5 mm. Successivamente, sono collocate nell'essiccatore, alla temperatura di 105ºC per 3 ore.

Come precedentemente anticipato, risulta chiaro, guardando i dati, che il SS è una biomassa molto più complessa da pirolizzare, poichè riporta un'alta percentuale di umidità, di inerti ed un potere calorifico basso.
Inoltre, quello che rende questa sfida ancora più difficile è la variabilità della sua composizione, che può essere soggetta a continui cambiamenti, causati dal passaggio di stagione, dalle tecnologie usate dall'impianto di depurazione da cui è originata, dallo stoccaggio, e

Tabella 1: Proximate analysis e ultimate analysis per il pellets in legno e il SS.

Proximate analysis				
	moisture [%]	volatile[%]	fixed carbon [%]	ash [%]
Wood Pellets	4,75	80,21	19,22	0,61
Sewage Sludge	8,18	54,10	2,36	35,36
Ultimate analysis				
	C [%daf]	H [% daf]	N[% daf]	O [% daf]
Wood Pellets	50,7	5,9	0,2	43,0
Sewage Sludge	30,8	5,3	4,5	59,4

dall'origine dell'acqua che affluisce al depuratore.

Materiali di riempimento

I materiali selezionati sono tutti minerali a basso costo, che presentano caratteristiche tra loro molto differenti, sia per quanto riguarda la morfologia, che per le proprietà chimiche dei siti attivi presenti sulla loro superficie.
Essi sono: dolomite, allumina, sepiolite, olivina e sabbia silicica. Quest'ultima è considerabile non attiva , ed è riportata come termine di paragone per confrontare il grado di attività delle altre.
Inoltre alcune prove sono state condotte con un catalizzatore al Ni- γAllumina.

Gli effetti che questi tipi di catalizzatori possono avere sulle reazioni di pirolisi, sono ampiamente discussi in letteratura. Quelli che reputiamo di maggiore interesse sono: l'aumento della resa del bio-olio,la diminuzione dei composti ossigenati nei volatili e l'incremento del rapporto H/C.

Altro aspetto preso in considerazione è il fenomeno di disattivazioine, che colpisce questi materiali dalle proprietà catalitiche, causato principalmente da covering, coking e avvelenamento.

Per ciascun materiale è tracciata la distribuzione granulometrica e la curva cumulativa, Figura 2.8. La frazione con particelle comprese nel range 250-425 μm, appartenente, secondo la classificazione di Geldart alla categoria *sand-like*, è separata per setacciamento e sono misurati la densità apparente, di bulk,la porosità e l'area superficiale esterna e totale (BET).

Verificati questi parametri, è calcolata la massa di minerale necessaria per ottenere il letto di riempimento di altezza, h_b, pari al diametro del reattore d_i ($h_b/d_i = 1$).

Per assicurare confrontabilità tra i vari materiali, è necessario che operino tutti nel medesimo regime di fluidizzazzione, fattore particolarmente influente nelle razioni condotte in un FBR.

Ciascun materiale presenta una diversa velocità di minima fluidizzazione U_{mf}, parametro dipendente dalla geometria delle particelle del materiale stesso e dalla temperatura.
Per calcolare tale valore alla temperatura operativa (T_{pyr}), è stato necessario utilizzare l'equazione di Carman-Kozeny, Eq 2.1, la cui validità è stata accertata sperimentalmente per ogni materiale, seguendo la metodologia adottata da Soria-Verdugo et al.[72].
Quindi, la U_{mf} è stata maggiorata di un valore fisso, $U - U_{mf} = 9cm/s$, ripreso dallo studio di ottimizzazzione precedente [16], per ottenere una fluidizzazione a bolle spinta, ottenendo U, la velocità del gas fluidizzante da usare nell'esperimento.
I valori ottenuti sono riportati nella Tabella 3.1.

Experimental setup

Lab-scale FBR

L'esperimento è stato svolto in un reattore a letto fluidizzato (FBR) cilindrico, in acciaio inossidabile, opportunamente coibentato, operante a pressione atmosferica e presentante un'altezza 10 volte il suo diametro, per evitare la dispersione del letto di riempimento durante la sua fluidizzazione.
Al suo interno è presente una termocoppia per la misurazione della temperatura, durante lo svolgimento dell'esperimento, mentre il fondo presenta una serie di fori per permettere l'immissione del gas di fluidizzazione omogeneamente su tutta la sezione del cilindro.
Per giungere alla temperatura prefissata, il dispositivo è fornito di 3 resistenze elettriche, capaci di fornire una potenza termica di 1,2 kWh.
La perdita progressiva di peso di biomassa, viene registrata da una bilancia di precisione, sulla quale è posto il reattore stesso, Figura 1. Gli agenti di fluidizzazione scelti sono l'aria compressa e l'N_2, che possono essere alternati tra loro a mezzo di una valvola manuale.

Analisi del segnale

Il segnale ottenuto dalla bilancia di precisione, fornisce la massa totale di bio-olio e gas rilasciati durante l'esperimento.

$$\frac{dm}{dt}_{vol} = \frac{dm}{dt}_{gas} + \frac{dm}{dt}_{bio-oil} \tag{1}$$

Tuttavia, a causa del flusso di N_2 mandato in continuo dal fondo dell'apparecchiatura durante la registrazione, il segnale presenta un rumore di fondo considerevole. Per attenuare tale disturbo, è usato un filtro adoperante la media mobile, che agisce come mostrato in Figura 3.2.

Per studiare la cinetica della reazione è stato adottato un modello di reazione semplificato del primo ordine che prevede un solo componente, la biomassa stessa.

$$\frac{dm}{dt} = -km_{vol}(t)^n \tag{2}$$

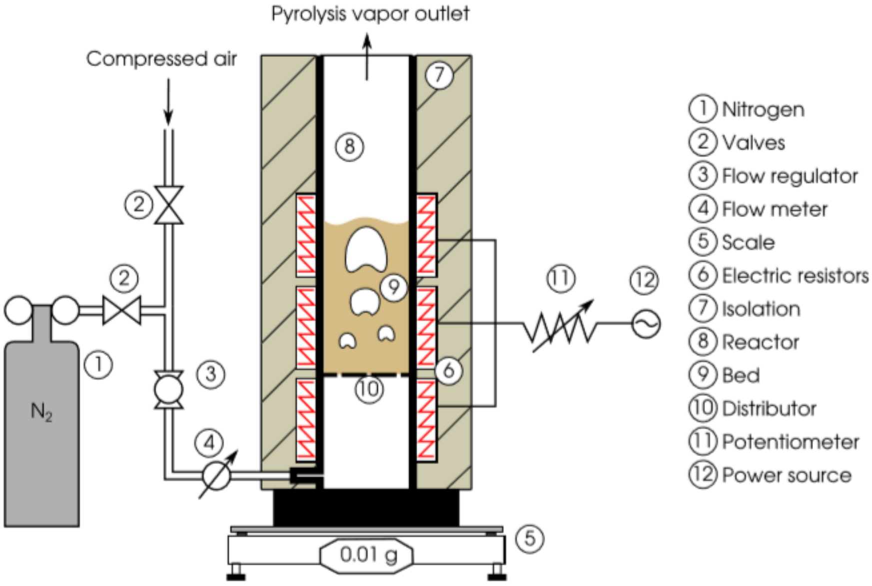


Figura 1: Schematic of the experimental facility. [72]

È calcolata la costante cinetica apparente k, dalla regressione dell'Eq3.8, e utilizzata per la formulazione del modello esponenziale a descrizione della progressiva perdita di massa, Eq 4.

$$ln(m_{vol,0}) - ln(m_{vol}(t)) = kt \tag{3}$$

$$m(t) = (m_0 - m_{vol,0}) + m_{vol}e^{-kt} \tag{4}$$

Il modello descritto risulta essere un'approssimazione accurata dei dati sperimentali (dalla valutazione del coefficiente di correlazione, R^2) se si trascurano la parte inizale (conversione fino a X=10%) e quella terminale della reazione.

Tale segnale viene tagliato quando la perdita di peso diventa pressocchè stabile, in corrispondenza del peso m_{fin} 5:

$$m_{fin} = m(t_{fin}) \tag{5}$$

$$\left(\frac{dm}{dt}\right)_{t_{fin}} = 0{,}0005 \tag{6}$$

Rendendo possibile il calcolo della resa totale di volatili 3.12.

$$Yield = \frac{m_{vol}}{m_0} = \frac{m_0 - m_{fin}}{m_0} \tag{7}$$

Solo inoltre tracciati il profilo della conversione e della reattività, e calcolato il tempo della pirolisi t_{pyr} (X=95 wt%). È possibile trovare le loro definizioni nei sottoparagrafi 3.4.1, 3.4.1.

Anche il segnale inviato dalla termocoppia viene registrato e analizzato, tracciando il profilo della sua derivata. Le reazioni sono nella maggiorparte dei casi a comportamento endotermico, presentando una derivata della temperatura nel tempo negativa. Tuttavia sono registrabili alcune eccezioni in cui le reazioni presentano un tratto esotermico, con derivata positiva. Per discutere di tali risultati, così come descritto nel sottoparagrafo 3.4.1, farò riferimento con:

- y_{min} al punto in cui la temperatura diminuisce con velocità maggiore, corrispondente al punto di minimo della derivata della temperatura $y_{min} = \frac{dT}{dt}_{min}$,
- $y_{cooling}$ al punto in cui la temperatura diminuisce più lentamente, corrispondente alla fase finale dell'esperimento, quando ormai la reazione è cessata e non si ha più conversione della biomassa. Questo parametro è corrispondente al punto di minimo del valore assoluto della derivata della temperatura $y_{cooling} = \left|\frac{dT}{dt}\right|_{min}$;
- y_{max} al punto in cui la temperatura aumenta con velocità maggiore, corrispondente al massimo della derivata $y_{max} = \frac{dT}{dt}_{max}$.

Procedura dell'esperimento

La procedura condotta per eseguire l'esperimento può essere così riassunta:

Raggiungimento della temperatura prefissata - è ottenuto mantenendo le resistenze a regime, utilizzando aria come agente fluidizzante, e monitorando l'innalzamento della temperatura fino ad un valore di circa 20 ºC superiore a quello a cui sarà effettuata la reazione di pirolisi;

Conversione della biomassa - una volta raggiunti ˜570ºC le resistenze vengono disconnesse dal reattore, il quale è posto sulla bilancia di precisione. Il flusso d'aria viene azzerato e la bilancia tarata. Successivamente, l'N_2 è sostituito all'aria, la portata necessaria regolata, e la registrazione del peso avviata. Una volta che i 550ºC saranno raggiunti, la biomassa è tolta dall'essiccatore, dove è conservata, e versata dall'alto nel reattore. La registrazione del peso continua finchè il valore del peso non si stabilizza.

Raffreddamento reattore e recupero del bio-char - terminata la reazione di pirolisi, il flusso di N_2 viene ridotto e il reattore lasciato a raffreddare, fino al raggiungimento di ˜100ºC. Il letto raffreddato è quindi estratto dal reattore e setacciato per dividere il bio-char dal materiale sabbioso. Il bio-char sarà poi destinato a successive analisi, quali la BET e la calorimetria.

Per dimostrare la ripetibilità del metodo, per ogni materiale sono condotte 4 prove, ottenendo sempre uno scarto quadratico medio minore di 1.

Influenza del fenomeno di disattivazione sui catalizzatori

Come precedentemente preannunciato, sono condotti due tipi di cicli per valutare la resistenza dei materiali al fenomeno della disattivazione: uno per studiare gli effetti derivanti dalla deposizione di char sulla superficie del materiale, e un secondo per analizzare quelli provocati dalla deposizione di ceneri.

Ciclo uno: deposizione di char

La procedura eseguita per questo esperiento è molto simile a quella precedentemente descritta, con la differenza che a fine reazione il letto fluidizzato raffreddato e setacciato, è collocato nuovamente nel reattore, per eseguire una nuova prova.
Inoltre, l'agente fluidizzante durante la fase di riscaldamento del reattore non è l'aria, ma l'N_2, per evitare che avvenga la combustione del char.
Seguendo questa procedura sono stati analizzati la sabbia, la dolomite e la sepiolite, per un totale di 10 cicli ciascuno.

Ciclo due: deposizione di ceneri

Il secondo ciclo presenta come unica variazione rispetto al primo ciclo l'agente fluidizzante: durante la fase di riscaldamento viene usata l'aria, e non l'N_2.
In questo caso, infatti, la combustione del char che si deposita sul materiale dopo ogni pirolisi, è un fenomeno voluto.
È da specificare che la temperatura a cui si giunge in fase di riscaldamento è di soli 20 ºC maggiore di quella a cui si effettua la reazione stessa, ed è mantenuta per soli pochi minuti, quindi si è ben lontani dalle condizioni per cui si può ottenere una rigenerazione del catalizzatore.

Proprio per valutare in maniera più approfondita il fenomeno, è stato condotto, per la sola dolomite (materiale presentante il grado di attività più accentuato e che maggiormente ha risentito della disattivazione), una rigenerazione completa in corrispondenza del decimo ciclo.
Il tattamento di rigenerazione è stato effettuato mantenendo il materiale per 3 ore in fornace alla temperatura di 650 ºC. Successivamente sono condotte altre 4 prove per verificare, l'andamento dei vari parametri tenuti in considerazione.

Accumulo di biochar

L'ultimo esperimento svolto, si pone come obiettivo quello di valutare l'effetto che ha l'accumulo di bio-char nel reattore.
Questa volta, la procedura non prevede il setacciamento del letto fluidizzato tra una ripetizione e la successiva: una volta che termina la registrazione del peso, il reattore è diretamente scaldato e riportato alla temperatura operativa per effettuare una nuova pirolisi, (senza il raffreddamento tra una ripetizione e l'altra).
L'unico agente fluidizzante utilizzato è l'N_2.
Seguendo questa procedura sono state ripetute 5 serie con il pellet e 5 con il SS. Sono state usate entrambe le biomasse poichè i due bio-char derivanti potrebbero avere effetti differenti tra loro, e uno degli obiettivi è proprio di verificare tali diversità.

Discussione dei risultati

Confronto tra i materiali

Per analizzare i risultati ottenuti, per ogni prova sono state tracciate le curve relative alla perdita di peso, il profilo della temperature e della sua derivata, la conversione e la velocità della reazione nel tempo. Inoltre è stata calcolata la resa totale dei volatili, Eq.8, la costante cinetica apparente k, Eq. 2, come riportato nell'articolo [74] e il tempo di reazione t_{pyr} come fatto da Morato et al. [16].

$$Yield = \frac{m_{vol}}{m_{tot}} = \frac{m_{tot} - m_{fin}}{m_{tot}} \tag{8}$$

Analizzando i valori della resa, riportati nel grafico a barre, Figura 2, ottenuti dal primo esperimento per entrambe le biomasse, risulta evidente che il pellets in legno ha riportato in ogni caso rese maggiori (~20 wt%) rispetto al SS.

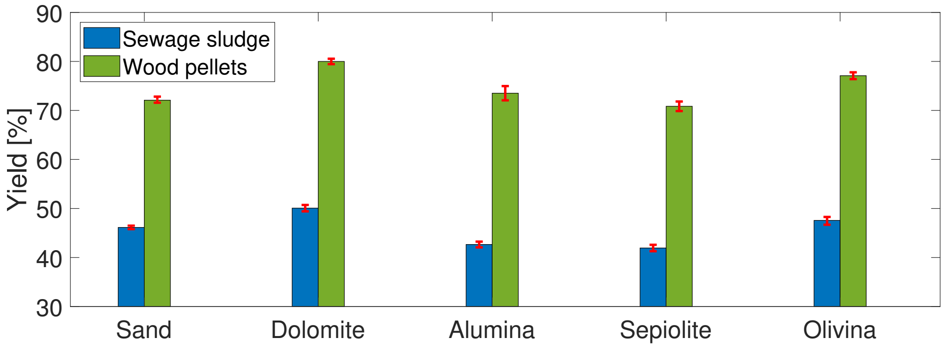


Figura 2: Confronto delle rese ottenute dalla pirolisi delle due biomasse, registrate conducendo l'esperimento con diversi letti fluidizzati: sabbia, alumina, sepiolite, dolomite, e olivina.

La dolomite è il materiale che ha dimostrato le migliori performance con entrambe le biomasse, pellets in legno e SS, riportando le rispettive rese di 80 wt% e 52,5 wt%, seguita dall'olivina con 77 wt% e 47 wt%.
Il peggior materiale per entrambe è risultato essere, la sabbia silicica, ottenendo rese del 72 wt% nel caso del pellets e del 43 wt% per la SS.
Invece, l'allumina e la sepiolite, si sono mantenute comunque molto basse, riportando valori di poco superiori a quelli della sabbia silicica.

Considerando la cinetica di reazione, si può innanzitutto affermare che il modello cinetico proposto risulta essere adeguato a descrivere la maggior parte delle reazioni, ottenendo un'approssimazione migliore per il SS piuttosto che con il pellets in legno. L'olivina risulta essere l'unico materiale che riporta uno scarto quadratico medio superione allo 0,8.

La dolomite è il materiale capace di ottenere nel caso del SS le migliori performance, con k di 0,195 1/s ed t_{pyr} pari a ~24 s, al contrario, l'olivina risulta essere il peggiore, con k di 0,08 1/s ed t_{pyr} pari a ~45 s.

Dimensione delle particelle di biomassa

Per avere un'idea di quanto possa influire la dimensione delle particelle della biomassa, pellets in legno non triturato è stato sottoposto allo stesso esperimento discusso nel paragrafo precedente. Come è possibile verificare dalla Tabella 4.3 sia la resa che la k sono risultate molto più basse rispetto a quelle ottenute con particelle di pellets in legno appartenenti al range 1-2.5 mm. Si sono registrate rese più basse dei circa 10-15% e k minori di circa 65-70%, a seconda del materiale utilizzato.

Fenomeno di disattivazione

Deposizione di char

Il primo ciclo condotto per lo studio della disattivazione si pone come obiettivo l'analisi degli effetti che può avere il bio-char depositatosi sulla superficie dei materiali di riempimento (coking).
Dalle foto scattate al materiale tra una ripetizione e l'altra, Figura 4.15, e Figura 4.16, si osserva il progressivo inscurimento del materiale, passando dal beige chiaro al nero.

Per ogni materiale, tutte le rese ottenute durante le varie ripetizioni, sono state riportate in un unico grafico, Figura 3, semplificandone la comparazione. La sepiolite sembra essere l'unico materiale che non risente di questo fenomeno, mentre la sabbia e la dolomite seguono due trend completamente diversi: le rese ottenute con la sabbia aumentano, passando da 74 a 80 wt%, quelle relative alla dolomite invece diminuiscono, da 82 a 76 wt%.

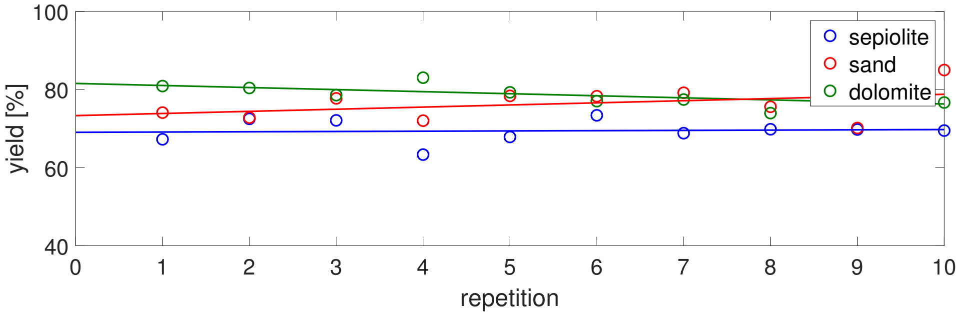


Figura 3: Pellets pyrolysis: First cycle. Comparison of the yields using respectively sand, sepiolite ad dolomite

Deposizione di ceneri

Il secondo ciclo invece, si propone come obiettivo quello di verificare eventuali fenomeni di covering e/o avvelenamento del materiale di riempimento.
In Figura 4 sono riportate le rese risultati dal primo e dal secondo ciclo, ottenute utilizzando la sabbia come bed material.
Si evidenzia che la sabbia, essendo un materiale che non presenta siti attivi sulla sua superficie, non è colpita dal fenomeno di disattivazione. Del tutto differente è il risultato ottenuto dalla dolomite, Figura 5 la quale è fortemente colpita dalla disattivazione, riportando una diminuzione della resa ancora più brusca che nel caso della deposizione di char.
In realtà sembra che tale abbassamento sia più marcato nei primi 4 cicli, e che poi continui in modo quasi parallelo al caso precedente.
Solo per la dolomite è stato ritenuto utile tracciare anche l'andamento della k, riportato in Figura 6: anche la cinetica è rallentata a causa dalla disattivazione.
Dopo la decima ripetizione, il materiale è stato sottoposto a rigenerazione, evidenziando un immediato cambiamento nel colore 4.18. Inoltre, da entrambi i grafici si può vedere che successivamente al trattamento termico, sia la resa che la k hanno registrato un incremento, seppur non raggiungendo i valori iniziali.

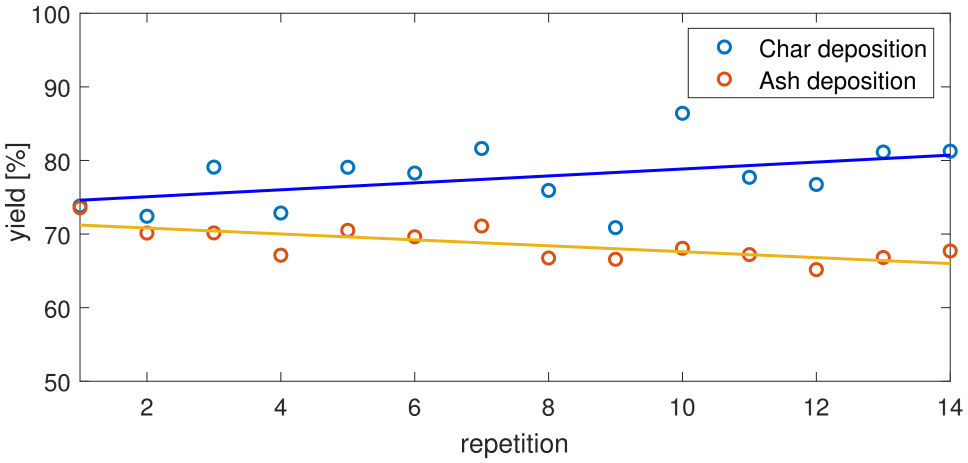


Figura 4: Bed material: sabbia. Confronto delle rese ottenute dal ciclo 1 e dal ciclo 2

Accumulo del biochar

L'ultimo ciclo condotto, è volto all'analisi di eventuali effetti provocati dall'accumulo di bio-char nel FBR.
Sono stati eseguiti con entrambe le biomasse, SS e pellets in legno, usando come materiale di riempimento la sabbia silicica.
La resa risulta rimanere stabile al procedere del ciclo, come evidenziato nella seguente tabella, Tabella 2. Tuttavia, osservando i profili della temperatura e le loro derivate, Figura

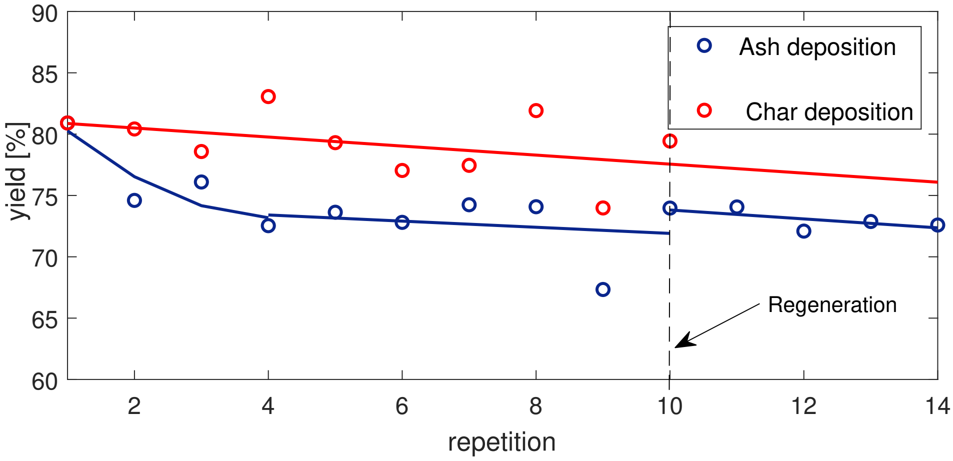


Figura 5: Confronto delle rese ottenute dal ciclo con deposizione di ceneri e di bio-char, utilizzando come biomassa il pellets in legno. Materiale di riempimento: dolomite

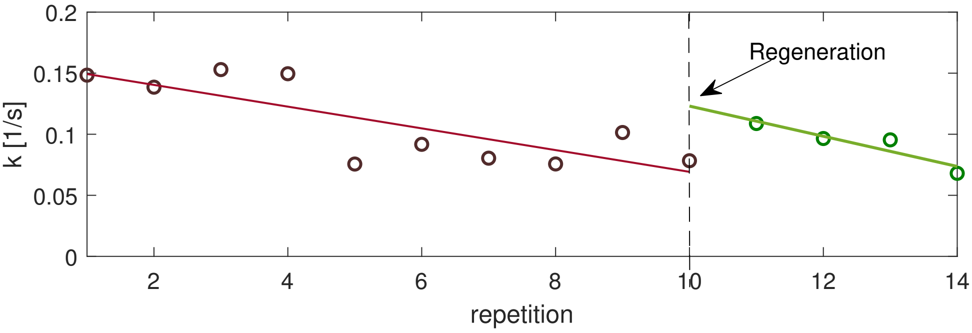


Figura 6: Confronto delle k ottenute dal ciclo con deposizione di ceneri e di bio-char, utilizzando come biomassa il pellets in legno. Materiale di riempimento: dolomite

4.24 e Figura 4.23, è possibile notare che, all'aumentare del bio-char nel sistema, si registrano diverse mutazioni degli andamenti di temperatura e della reattività, ad indicare la presenza di una ipotetica attività catalitica.

In generale, ripetendo il processo con una quantità maggiore di char (materiale con una capacità termica specifica non trascurabile), è normale aspettarsi che il sistema presenti un'inerzia termica maggiore, traducibile in un rallentamento nei tempi di raffreddamento. Infatti, analizzando le $y_{cooling}$ ottenute in entrambi i cicli si può notare una progressiva, anche se minima, diminuzione.

Il trend riportato dalla $y_{cooling}$ è invece del tutto differente. Nel caso del pellets, si osserva che in corrispondenza della reazione, si registra un progressivo rallentamento nel raffreddamento del sistema, man mano che si accumula il bio-char nel sistema. Ciò potrebbe essere spiegato ammettendo la presenza di attività catalitica da parte del biochar,

Tabella 2: Resa dei volatili ottenuta dalla pirolisi delle due biomasse, eseguendo il ciclo con accumulo di bio-char.

Cycle	1	2	3	4	5
Yield [%] (Pellets in legno)	72,0	68,0	74,0	68,0	70,0
Yield [%] (SS)	45,3	41,3	42,3	47,5	46,9

promuovendo, tuttavia, reazioni nel complessivo meno endotermiche.

Completamente opposto è il trend ottenuto ripetendo l'esperimento con il SS. Infatti, in questo caso, la reazione diventa sempre più endotermica, registrando un'accelerazione della velocità di raffreddamento del sistema in corrispondenza della reazione. Dal calcolo e dalla rappresentazione grafica della k, si può notare che in entrambi i casi si registrano diminuzioni della velocità della reazione, ma molto più marcate nel caso del pellet in legno, piuttosto che con il SS, Figura 7.

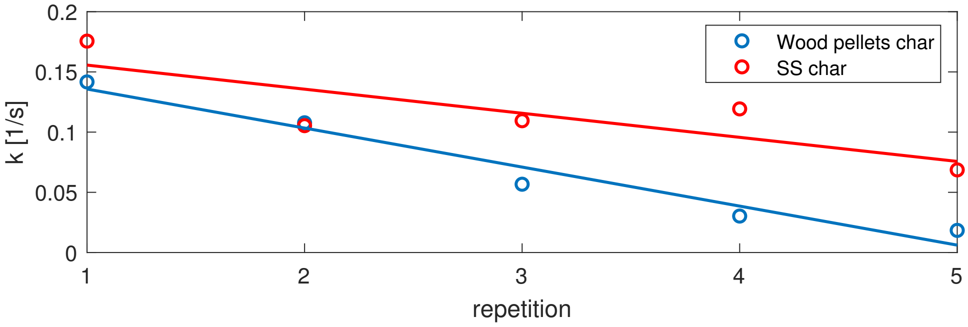


Figura 7: Confronto delle k ottenute eseguendo il ciclo con accumulo di bio-char, con pellets in legno e con SS.

Effetto catalitico del $Ni - \gamma Al_2O_3$

Anche il $Ni - \gamma Al_2O_3$ è stato testato come potenziale catalizzatore nel FBR. Tuttavia i rusultati ottenuti non sono stati quelli sperati: la resa che ne è risultata, sia nel caso del pellet in legno che del SS, è stata inferiore a quella ottenuta utilizzando la sabbia silicica (rispettivamente 62,7 wt% e 46,5 wt%).

Il modello risulta essere ben approssimabile a quello di primo ordine proposto, ottenendo k confrontabili a quelle ottenute con gli altri materiali, Tabella 4.8.
Riguardo la temperatura, la reazione è endotermica con entrambe le biomasse, più marcatamente con il SS, Figura 4.28.

Conclusioni

La reazione di pirolisi è risultata essere fortemente influenzata dalla presenza dei catalizzatori proposti, incrementando la resa di ~10 wt% .
La dolomite è risultato essere il materiale più vantaggioso, anche sotto il punto di vista della cinetica, riportando la migliori performance in termini di t_{pyr} e di k.
Tuttavia ha presentato lo svantaggio di essere fortemente soggetta a fenomeni di disattivazione, soprattutto per covering e avvelenamento dovuti alla deposizione superficiale di char e ceneri.
Sperimentalmente è stato provato che è possibile effettuare un parziale recovering con un trattamento termico di rigenerazione, che tuttavia non riesce a ripristinare completamente le prestazioni iniziali.

L'olivina ha ottenuto buone rese, ma cinetiche e tempi lenti. Ha riportato un comportamento esotermico sul finale della reazione: sarebbe interessante approfondire gli studi su questo materiale per analizzare anche la composizione dei volatili e verificarne una eventuale capacità di migliorare la qualità del bio-olio.

All'aumentare della dimensione delle particelle di biomassa, le cinetiche della reazione sono diventate 3 volte più lente, la resa più bassa del circa 10-15% e i tempi della reazione raddoppiati.

Il bio-char si è dimostrato una potenziale alternativa ai catalizzatori convenzionali per operazioni di upgrading in situ (riportando un inceremento della resa del 10%), non essendo soggetto alla disattivazione, e producendosi spontaneamente durante il processo stesso.

Alcune considerazioni possono essere fatte riguardo possibili utilizzi del biochar prodotto: l'area superficiale totale (BET) non è risultata sufficianetemente alta per pensare ad un utilizzo diretto per la rimozione di inquinanti da correnti gassose, tuttavia, previa tratamento di attivazione, potrebbe essere destinato a tale funzione. In alternativa potrebbe essere utilizzato per la depurazione di acque o suolo, operazioni per le quali non si richiedono alte aree superficiali, ma sono di maggior interesse la presenza di gruppi funzionali superficiali, solitamente presenti sul bio-char.

Possibilità di sviluppi futuri

Una volta selezionato il materiale capace di offrire le migliori prestazioni, l'esperimento deve essere ripetuto in un impianto pilota, comprendente un impianto di condensazione, per poter separare la frazione liquida da quella gassosa.
Questo passaggio è di fondamentale importanza per consentire il calcolo della resa di liquido prodotto, e l'analisi delle sue proprietà fisiche e chimiche, come la viscosità, l'acidità, il PCS e la composizione.

Anche l'identificazione dei componenti presenti nella frazione gassosa potrebbe essere interessante: a tale scopo si può accoppiare all'impianto un GC-MS (gascromatografo con spettrometro di massa).

Per identificare la natura dei siti attivi presenti sulla superficie della dolomite, e i meccanismi alla base della sua disattivazione, il materiale dovrebbe essere sottoposto ad analisi spefifiche come BET, SEM-EDX, XRD, XPS, and TPO/TPD.

Contents

Chapter 1

Introduction

Pyrolysis is a thermo-chemical reaction, consisting in the transformation of solid biomass in liquid, gaseous and solid products, usable mainly as fuel. Considering the actual World request of clean forms of energy, it could become a viable alternative in the near future, alongside wind, solar, water and nuclear options [1]. Pyrolysis is a thermo-chemical reaction, consisting in the transformation of solid biomass in liquid, gaseous and solid products, usable mainly as fuel. The biomass that has been identified as the most suitable, is the lignocellulosic one, such as wood biomass, dedicated energy crops and agricultural residues [2]. In additon, there are some residues that can be also used for this purpose such as sewage sludge. However, the achievement of a process capable to pyrolyze sewage sludge in a proper and competitive way, might solve its disposal problem as well, pursuing an additional benefit. In fact, it provides to reduce up to 50% its volume, to its stabilization and to trap heavy metals in the char structure, resulting less sensible to lixiviation if compared with traditional methods [3].

Thought, even if it could seem an attractive option, technical challenges and problems of economic viability are actually impeding the spread of this technology [1]. One route to overcome this obstacles might be represented by the improvements of catalytic bio-oil upgrading, but until now, the number of researches focused on this topic are very limited. The ones existing are mostly based on previous studies, using lignocellulosic biomass: materials traditionally considered are zeolites and gamma-alumina [3]. From this perspective, to test and to compare new suitable types of catalyst, capable to facilitate the development of pyrolysis for sewage sludge, might result interesting.

1.1 Background

In the lasts decades, petroleum based fuel has been increasingly contested because it generates huge amounts of net carbon dioxide emission and other pollutants such as NO_x and SO_x, causing environmental problems: global warming, climate change and air pollution. Moreover, it is a no-renewable energy source and its supply is rapidly diminishing causing frequently and undesired fluctuation on the prize [4].

European Commission reports on the IPPC site that *"the challenges of producing and using energy resources sustainably and protecting our natural environment equally represent an opportunity to pursue sustainable economic growth, while contributing to climate change mitigation and adaptation."* [5]. The UE is adopting several policies as the last "Clean Energy for All Europeans package" that involves progressive fossil fuel substitution [5], issued to reach the target of 32% for renewable energy sources in the EU's energy mix by 2030. In fact, it is possible to read on the same site [5] that there is a strong will to promote the usage of renewable resources: *"Measures to increase the share of sustainable renewable energy sources in the energy mix can lower overall environmental and climatic pressures compared to other forms of energy"*. But, despite all, Europe still depends strongly by fossil fuel as reported in *the 5th International Conference on Energy and Environment Research*, ICEER 2018 [6].

Therefore there is an urgent need to find renewable and environmentally benign feedstocks for sustainable supply of fuels and energy. It is in this scenario where biomass could represent a viable solution:

- it is renewable, growing up rapidly and easily, just using the sunlight due to photosynthesis and metabolizing carbon dioxide from the atmosphere;
- it gives no net contribution to global greenhouse gas, considering that the CO_2 released during the combustion is equivalent to the amount absorbed recently by the plant itself during its life;
- its combustion produces much less SO_x and NO_x, containing itself less nitrogen and sulphur compared with coal or petroleum oil.
- it is a locally grown resource, resulting in a positive impact on the local economy and being relatively free from uncertainties on prize and storage.

It is important to specify that biochemical processing of biomass (fermentation) to produce ethanol and biodiesel, is already being pursued commercially on a large scale. But, only cereals (composed by starch and sugar) can be used for this purpose, which may be not sustainable if considered that it divers them from the grain market to the energy production. For this reason, the real goal would be to succeed in using ligno-cellulosic biomass (non-food) for fuel production, preferably if it offers, at the same time, the possibility to dispose a sub-product of a process, instead of using a fast-growing plant, plant with this purpose [4].

Staying at the actual data showed on the last Report drown up by ECOFYS [7], in Europe, the most exploited renewable resource is biomass, covering the 64,5 % among all, but the majority of it is used for the generation of heat, and it derives mainly from the urban waste. Instead, the consumption of liquid bioenergy carriers represents only the 11% of all bio-energy, or 1.2% of all renewable energy (in all sectors). It is mostly applied in transport sector (11.2 Mtoe biodiesel and 2.7 Mtoe bioethanol), but it also accounts for a small amount of so-called 'bioliquids', used for power production in conventional thermal power stations (1 Mtoe gross) and for heat and power in CHP stations (0.3 ktoe gross).

These bioliquids are monstly originated by vegetable oils and pyrolysis oil.

In the prospective of a future increase of this modest percentage dedicated to the bioliquid and biodiesel, the thermo-chemical (such as gasication and fast pyrolysis) route, among all the possible strategies for biomass conversion into available fuel, seems to be the best ones.

1.2 Thermo-chemical conversion process

Biomass conversion into useful fuel, can be achieved through two different paths: biochemical (fermentation) and thermo-chemical (pyrolysis or gasification) as it is shown in Figure 1.1. The biochemical conversion is the most ancient, developed and used: in the past it was adopted by India and China for methane production by anaerobic microbial digestion of animal wastes. Nowadays, most of the ethanol for automotive fuels is produced from corn using fermentation. It is a technology already completely developed, but it is limited to cellulosic biomass: ligno-cellulose can not be processed with this method. On the other side, thermochemical conversion is promising to overcome this obstacle, but it has been developed just recently, and it was used for the first time on large scale only during the Second World War, when a million of small biomass gasifiers have been build to supply at the increasingly request of energy. Peculiar differences are summarized in Table 1.1.

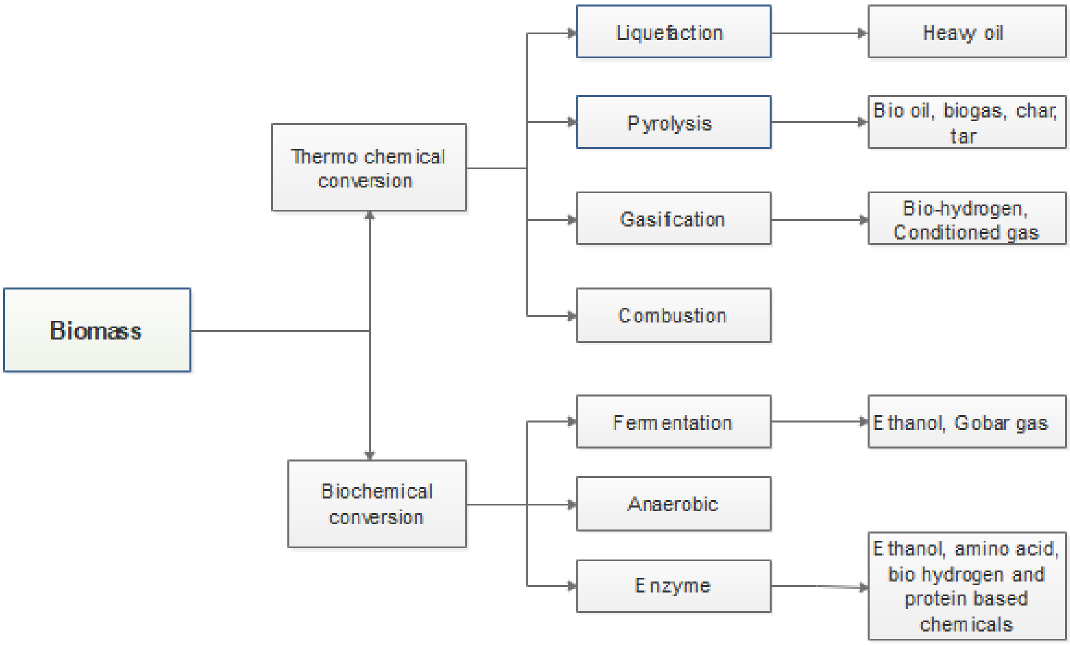


Figure 1.1: Routes for biomass conversion

Mainly, it is possible to distinguish four different pathways belonging to thermochemical

Table 1.1: Comparison of Biochemical and Thermochemical Routes for Biomass Conversion into Ethanol [4]

	Biochemical (sugarfermentation)	Thermochemical
Feedstock	Sugarcane, starch, corn	Cellulosic stock, wood, municipal solid waste
Reactor type	Batch	Continuous Reaction
time	2 days	7 minutes
Water usage	3.5–170 liter/liter ethanol	<1 liter/liter ethanol
By-products	Distiller's dried grain	Syngas/electricity
Yield	450 liter/ton	265–492 liter/ton
Technology maturity	>100 in U.S. plants	Pilot plant

processes: combustion, gasification, pyrolysis and liquefaction. Each of them is characterized by a determined range of temperature and a certain percentage of oxygen in the carrier gas:

Combustion is a strongly exothermic reaction which occurs between oxygen and hydrocarbons, producing more stable compounds as H_2O, CO_2, CO, exhaust gas. It requires very high temperature and oxygen excess. It is useful to produce heat.

Gasification is the conversion of hydrocarbons, fossil or not, into useful chemicals or gaseous fuel in order to improve its heat value, to remove sulfur or nitrogen or to reduce the hydrogen-to-carbon ratio. It requires a medium, such as gas or supercritical steam. It is achieved in oxygen deficit at high temperature.

Pyrolysis is a thermal decomposition of hydrocarbon macro-molecules into smaller ones, through endothermic reactions It is performed in total absence of oxygen and at medium-high temperature. The desired product is usable liquid fuel known as bio-oil.

Liquefaction converts solid biomass into liquid fuel and it can be done through pyrolysis, gasification as well as through hydro-thermal process. Biomass, placed in contact with water at relatively high temperature and high pressure, is transformed into an oily liquid.

The only thermochemical conversion that will be discussed in this thesis, is the pyrolysis, so, in order to better understand the mechanisms on which it bases, a brief resume of its main characteristics is provided.

1.2.1 Pyrolysis

Pyrolysis is a thermo-chemical decomposition of biomass into a range of useful products. Usually it is carried out in the total absence of oxidizing agents, and at relatively low temperature range, from 300 to 650 °C, if compared with the one used for the gasification (800 to 1000 °C) or combustion (higher than 1000 °C). During the pyrolysis process, large complex hydrocarbon molecules of biomass break down into relatively smaller and simpler molecules of gas, liquid, and char. Their nature depends on several factors, including pyrolysis temperature, heating rate, presence of catalyst, presence of moisture in the biomass and its particle size:

Char made mainly of carbon (in a range varying from 50wt% to 96wt%) [8], contains also a small amount of oxygen and hydrogen. A high lower heating value (LHV), around 32 MJ/kg, distinguishes it from the parent biomass and its liquid product [4]. The possible uses are varied, and they can range from carbon sequestration to soil fertility improvement and pollution remediation, for both water and air. More over, some catalytic utilization for high value applications has been tuned as well [8].

Bio-oil is a microemulsion in which the continuous phase is an aqueous solution of the products of the hemicellulouse, cellulouse and lignin fragmentation, while in the discontinuous one, pyrolytic lignin macromolecules are prevalent. In addition, is always possible to find some molecular fragments of cellulose, hemicellulose, and lignin polymers, which has not been pyrolyzed properly. Compared with char and the original biomass, it presents a lower LHV that can reach at the most 18 MJ/kg in wet basis. Its molecular weight may exceed 500 Daltons and it is obtained by a rapid quenching operation stopping the simultaneous depolymerization and fragmentation of cellulose, hemicellulose, and lignin, composing the biomass [4]. Due to its high instability caused by the presence of oxygenated compounds, and its low LHV it results impossible to use it as engine fuel without any successively operation of up-gradation [8].

Gas includes both condensable and uncondensable gases, such as CO_2, H_2O, CO, C_2H_2, C_2H_4, C_2H_6, C_6H_6, etc., which are originated from the decomposition and also reforming of carboxyl and carbonyl groups, Instead, H_2, also present, is originated by the reforming and decomposition of C –H groups and aromatics [8]. Its LHV can be very low (11 MJ/kg) for the gases originated from the primary decomposition, but quite high (20 MJ/kg) for the ones produced during the secondary phase of pyrolysis [4]. Reaction temperature, moisture content and biomass particles size can affect in a significant way gas composition. [8].

Pyrolysis process may be represented by the following generic reaction, although, how it easy to image, the entire reaction is composed by several sub-reactions which take place in two different moment of the process [8]:

$$C_nH_mO_p(Biomass) + heat \rightarrow \sum_{Liquid} C_xH_yO_z \sum_{Gas} C_aH_bO_c + H_2O + C(Char) \tag{1.1}$$

Primary reactions leads to the formation of char and condensable gases. They are the first ones to be carried out:

- **Charring** leads to the formation of char, which is an aromatic polycyclic carbon resulted from combination or condensation of benzene rings.

- **Depolymerisation** involves the cracking of the bond linkages between the monomers. During the entire process, it is dominant reaction routes, which result in the production of volatiles and the gases.
- **Fragmentation** provides the breakage of covalent linkage bonds of the unit monomers and polymer. Components with short chain and some non-condensable gases are produced during this step.

Secondary reactions take place thanks to the primary compounds, that are not stable, and the char, which acts as a catalyst, promoting the formation of liquid, uncondensable gases and additional char,

- **Cracking** occurs into the homogeneous gas phase, where condensable vapor is cracked into non condensable permanent gases.
- **Recombination** takes place in both, the homogeneous gas phase, where small molecules reacts between themselves, producing heavier compounds (bio-oil), and in the heterogeneous gas-solid phase, where phenomena of deposition appears on the solids surface, promoting formation of further char.

Mentioned reactions can be both endothermic and/or exothermic. According to several researchers, cellulose pyrolysis is endothermic, but lignin pyrolysis is exothermic. Wood pyrolysis is exothermic and the main cause of heat generation is the secondary decomposition of volatiles, possibly catalyzed by the remaining solid.

Depending on the chosen parameters, pyrolysis can proceed in three different ways: slow, intermediate, fast and flash pyrolysis.

Flash pyrolysis has, as objective, to maximize the gas production. It provides a quench operation collocated just after the reactor, where an intimate and fast contact between biomass and heat carried is ensured. To achieve proper conditions, they are heated separately and then conduced to the mixer where the reaction is run. The temperature used is very high (around 1000 °C for the gas and 600 °C for the liquid) [4].

Fast pyrolysis is used if the target of the process is the bio-oil and its yield can reach up to 75 wt%. It is possible to achieved to this purpose by limiting the residence time of the vapors in the reactor. In fact, its design is focused on the quick removal of the formed volatile products from the hot solids still present in the reactor, avoiding further reactions which involve formation of secondary products. Moreover, always for the same scope, small biomass particle sizes is adopted to ensure high heat and mass transfer. Usually, the reaction takes only few seconds (0,5-10 s) and it runs in the temperature range of 450–600 °C [1].

Intermediate pyrolysis is focused on enhancement of char quality. Reducing the production of high molecular tar, is possible to obtain dry and brittle char, more adequate to further utilization, such as carbon sequestration and fertilization. The reactor used, consists in two coaxial conveyor screws: the outer screw transport the biochar, which serves as heat carrier. This design provides moderate residence time of the biomass in the system and operates at temperature range of 400-550 °C. Recommended particle size is bigger than the one used in the fast pyrolysis, an this simplifies the subsequent char separation [1].

Slow pyrolysis gives char as principal product. It is characterized by long residence time, slow heating rate (0,1-2 °C/s) and low temperature if compared with the previous cases described (around 400 °C). Usually the small amount of bio-oil and gas produced are not collected, with consequential environmental impacts [1].

1.3 Pyrolysis technologies

Biomass is feed into the reactor, where the needed temperature is set. So, decomposition of the material starts (Figure 1.2): condensable and non-condensable vapours leave the pyrolysis chamber, while the produced char remains partially in the reactor and partially, as small particles, in the gas. The gaseous stream is cooled down, after that the char has been separated, obtaining the liquefaction of bio-oil. Instead, the remaining non-condensable components might be used to heat up the reactor by their combustion or used as direct heat carrier, through their re-circulation to the pyrolysis chamber. Otherwise, they can be destined to further chemicals production. For the solid can be made a similar choice: it can be used as thermal source or considered a commercial sub-product of the process [4].

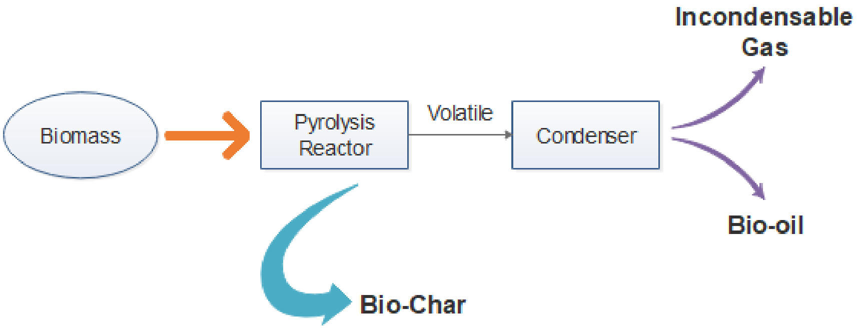


Figure 1.2: Schematic for pyrolysis process

1.3.1 Pre-treatments

In some cases, can be very useful to undergo some pre-treatments on the biomass to improve the yield or the quality of the bio-oil produced:

Physical pre-treatments , include all the processes which do not provide chemical reactions, and are always easy and economic. The most common are the reduction of particle size, the densification and the moisture removal.

- Reduction of particle size is quite useful because improve heat and mass transfer of the system, influencing the reaction rate and simplifying the volatilization of light compounds,

- Densification can affect both the composition and the yield of the products, Common equipment are the pellet mill, briquette press, and screw extruder.
- Moisture removal has the objective of reducing the required energy for the pyrolysis process.
- Steam explosion has the effect to make polymers of biomass fiber more accessible, breaking tight packed cellular structures and simplifying subsequent steps.

Chemical pre-treatments are provided in order to limit the development of undesirable effects caused by inorganic minerals possibly presents in the biomass.

- Acid and alkali pre-treatments have to neutralize carbonates, phosphates, sulphates and chlorides usually present in the biomass, which may cause increase of corrosiveness, acceleration of aging process and catalysation of char formation.
- Hydrothermal pre-treatments are employed to increase the carbon and energy content of biomass, producing compounds such as acetic acid, pentoses, hexoses, furfural, phenolic compounds. It is performed setting the temperature of 18–260 °C and the pressure up to 4.69 MPa.

1.3.2 Reactors

To optimize the process, it is necessary to evaluate carefully the reaction parameters, because each of them can have a particular effect on the production. In any pyrolysis process, the most important facility is the reactor, on which directly depends the heating system. Several reactors have been designed in the last two decades to improve the performance of the pyrolysis, and they can be briefly summarized in the following categories [8]:

- Fixed bed reactor is the oldest type of equipment used for the pyrolysis. It is characterized by slow residence time and very low heat transfer, leading to high char production [9];
- Fluidized bed reactor (FBR) is the most considered in research and until now, it seems to be the most successful, providing a high yield of desired products[10]. It is the most suggested to performed fast pyrolysis and it can ensure a good heat and mass transfer, giving a high quality bio-oil, and limiting the carryover of char in the liquid [4]. It is characterized by a simple design, easy scale-up, and proficient control over the residence time. However, some disadvantages are present, such as large reactor size, and the high cost of construction and operation [2].
- Circulating fluidized bed (CFB) and transported bed reactors use both, carrier gas and fluidized bed material, to provide the necessary heat to the reaction. Heat transfer is ensured by both convection and conduction. The required biomass particle size should be smaller than 3 mm [4].
- Rotating cone reactor uses centrifugal force to ensure intimate contact between biomass and heat-carrier solid particles, providing a good heat transfer. This equipment requires very short residence time of the biomass, and it is not necessary a carrier gas. The only issues may be the scale up of the reactor, considering the complexity of the geometry [4].

- Ablative reactor do not require a carrier gas, and the heat transfer is provided due to the direct contact between biomass particles and the hot surface. It gives the possibility to use large particle size, but it needs long residence time, giving low conversion and a high contamination of the liquid product by the carbon particles [9].
- Screw or auger reactor is one of the newest technology developed. It is the only equipment that gives the possibility to switch from slow to fast pyrolysis. It performs biomass heating by mixing it together with a solid heat carriers, using a screw [11].
- Vacuum reactor is designed to transfer the heat to the biomass particles by direct contact with a hot surface. The reaction do not necessitate of long residence time and large particle size can be used. However, this equipment does not provide a good heat and mass transfer and requires large scale size [9].

Despite a huge variety of reactors exists in literature, none of them is mature for an effective commercial use [1].

Pyrolysis can be performed using several inert carrier gas, which carry up to different results in yield and composition, affecting the reaction mechanisms. Gases mostly used are N_2 , H_2 , CO, CO_2 , CH_4 and steam. Staying at the last researches, the one capable to give the highest yield of bio-oil is CH_4 while the lowest one is achieves by the CO, presenting a gap of 10 wt%. Thought, CO promotes the production of more stable bio-oil, reducing the methoxy- compounds. Instead, steam increases the yield of organic oxygenates by preventing some secondary reactions, CO_2 originates a char rich in carbon and H_2 ensures an increase of the heating value of the derivative fuel [8].

The temperature is another peculiar variable. Several studies has been provided to evaluate its impact: at low temperature is possible to detect primary rearrangements as water elimination, bond breakage, appearance of free radicals, formation of carbonyl, carboxyl and hydroperoxide groups. Increasing it, other reactions take place, involving the production of char, bio-oil and gases. Once that 600 °C is passed, decomposition of char starts, producing carbon-rich residual solid forms [8]. So, it is quite important to calibrate opportunely temperature and heating rate, searching for a good compromise between yield, quality and cost.

The same consideration can be done on the choice of residence time of the vapor, which is another fundamental parameter: for short residence time is possible to obtain high bio-oil production, but if it is too short there is the risk that complete decomposition is not achieved [8].

1.3.3 Upgrading processes

To commercialize the bio-fuel and produce it on big scale, it is necessary to resolve some challenges still present. Indeed, produced bio-fuel should have physical and chemical characteristics compatible with petroleum fuel, gaining the possibility to be used as engine fuel. However, it has some undesirable proprieties, which impede its utilization without further upgrading as high corrosiveness, thermal instability, low aromatic hydrocarbon, high oxygen content and low heating value [12]. More over, bio-oil is subjected to aging, which is a physical phenomenon linked with its multiphase microemulsion nature [12], in which oligomers form aerosols, leading to the formation of more water, to the increase of viscosity and phase separation [13].

Nowadays, the trend is to use catalytic technologies, which can be sub-divided in two main groups: improvement of bio-oil quality after that the process has taken place (ex-situ solution), or directly inside the reactor (in-situ solution).Ex-situ upgrading is performed with metallic or bifunctional catalysts in hydrotreating processes (using H_2 atmosphere under high pressure). The most used catalysts are the cobalt–molybdenum, nickel–molybdenum and their oxides supported on Al_2O_3 [14]. The catalyst is placed in a secondary reactor downstream from pyrolysis chamber. It can operate under different conditions than those of the pyrolysis.In-situ upgrading is performed directly inside the reactor (fluidized or fixed bed reactor), so the catalytic material is subjected to the same condition of the pyrolysis chamber. Usually, for the processes, non-renewable and cheap disposable material are adopted such as zeolitic catalysts and mesoporous aluminosilicates which result very appropriate due to their high porosity and superficial acidity [14]. In both cases, catalyst can have several effects on the pyrolysis reaction [9]:

- Decomposition temperature decreases, with consequential increase of the liquid yield;
- Deoxygenation of bio-oil is provided thank to decarboxylation, decarbonization and dehydration reactions, which releasing CO, CO2 and H2O, contributes to oxygen removal;
- Stabilization of bio-oil is registered, reducing polymerization precursors;
- Formation of coke due to dehydration reactions (mainly due to high acidity of catalysts) occurs.

Depending on the morphology and the nature of the catalyst is possible to obtain different selectivity and conversion, so it is becoming of peculiar importance to determine the differences among performances that each catalyst can show.

1.4 Challenges

Currently, staying at the available literature, pyrolysis process results to be in the early stages, in fact both reaction mechanisms and subsequently the reactor controlling system are not sufficiently developed, and the up scaling of the technology still result difficult. Even if several studies have been provided, taking in consideration a big amount of possible system designs, the real engineering limits of the emerging pyrolysis technology have not been exhaustively explored. Existing gaps can be summarized as follows [15]:

- Current cost of bio-oil do not result competitive, compared with fossil fuel;
- Supplies of bio-oil do not ensure an appropriate testing campaign and consequently, application development remains a problem;

- Standards for use and distribution of bio-oil are not complete;
- Accurate characterization and standardization of the bio-oil would be necessary to ensure a wide range of energy application;
- Produced bio-oil is not compatible with petroleum fuel;
- The market still shows skepticism toward usage of bio-oil;
- Lack of knowledge for environmental and safety issues is still existing;
- Promotion of pyrolysis as a technology that the public opinion could approve is proving to be complex;
- Scale-up of technology should be achieved, improving the number of researches focused on it.

Moreover, there are other issues linked with the presence of the catalyst, which is subject to rapid poisoning and deactivation, reducing its capacity of upgrading the bio-oil and improving the yield.

1.5 Scope of the thesis

The thesis is focused on the optimization of the pyrolysis of SS process, using an innovative method based on the measurement of the mass loss in a fluidized bed reactor, collocated on a precision scale, continuing the work previously carried out by Morato et al. [16].
In the previous research, the influence that nitrogen velocity, temperature and particle size have on the process, have already been studied. Now, adopting the suggested parameters from the previous work, we want to investigate on the potentiality of several low-cost materials used as fluidized bed.

The main objective is to individuate the bed material capable to give the best performance for the SS pyrolysis, compared with the ones obtained with wood pellets, considered, up to now, the most suitable biomass.
The proposed materials are olivina, alumina, sepiolite and dolomite which are considered all materials widely diffused in nature . In order to evaluate their suitability for this application, sand is also used as term of comparison.
Moreover, in order to better investigate on the viability of the chosen materials for this type of application, deactivation phenomena is studied, by submitting the materials to cycles promoting once the char deposition and once the ash deposition on its surface.

Produced char, from both the biomass, is also considered as a viable catalyst, and advantages and disadvantages are reported.
In addition, some possibilities for its future utilization are taken in consideration, submitting the samples to the BET and to the calorimetry analysis.

1.6 Outline of the thesis

This thesis presents an experimental research on the use of the SS as biomass feedstock, and minerals as alternative bed materials in a thermogravimentric FBR in N_2 bubbling fluidized bed

. It is composed of five chapters, summarized as follow:

In the first chapter it is possible to find an introduction to the general thermo-chemical process and specifically to the biomass pyrolysis. Its future applicability for the biomass disposal is discussed, reporting, also, all the challenges linked with this promising technology.

The second chapter is mainly divided in two parts: one is dedicated to the proposed biomass and to their characterization, while the second is focused on the introduction to the bed materials, and to the description of their characteristics, including a brief section reporting how their minimum fluidization velocity can vary and their deactivation tendency.

The third chapter describes the equipment, the material preparation, the method used to evaluate the minimum fluidization velocity and the kinetic model adopted to analysed the data. Moreover, the experimental procedure to evaluate the performances obtained by the different materials, to study the deactivation phenomenon, and the effects of the biochar accumulation are explained.

In the fourth chapter, obtained data are summarized, focusing particularly on the comparison of the yields, the apparent kinetic constant, the temperature profile, and the time of the pyrolysis between the different cases.

In the last chapter, the conclusion are reported, with in the proposal of future works for the continuation of the research.

Chapter 2

Materials

2.1 Biomass feedstock

Biomass composition is one of the factor that more affects pyrolysis process. In the last years, many types of researches involving the selection of the best biomass for pyrolysis, were carried out. Staying at what has been written in a review of 2018 [17] more than 100 different types of biomass have already been analyzed in order to find, for each biomass, the optimal value of the main parameters, such as particle size, heating rate, pyrolysis temperature, gas flow rate, rate feed, and holding time.

Biomass is composed of lignin, hemicellulose, cellulose and a small fraction of inorganic matter. Each type of biomass is characterized by a different fraction of these three components. But even in the same biomass, variation of the composition may occur, depending on soil, age or planting conditions [18].The quality and yield of pyrolysis products are strictly linked with the biomass composition and its variations. In general, the biomass with higher cellulose and hemicellulose contents produced a higher bio-oil yield than the biomass with high lignin content. In fact, lignin decomposition is difficult due to its greater structural stability, and it leads to a higher yield of char [19]. Moreover, according to Qu et al. [20], cellulose is more volatile than hemicellulose. Therefore, the material with the highest cellulose content leads to a higher oil yield.

Proximate analysis of the biomass is very useful, giving the possibility to distinguish volatile, fixed carbon, moisture, and a small amount of inorganic impurities known as ash.

The organic compounds are also subjected to ultimate analysis, to identify the four principal elements: carbon (C), hydrogen (H), oxygen (O), and nitrogen (N). Biomass (e.g., MSW and animal waste) may also have small amounts of chlorine (Cl) and sulfur (S). The latter is rarely present in biomass, apart for secondary sources like demolition wood, which comes from torn-down buildings and structures [4]. In general, it was observed that the higher volatility, heating value, amount of carbon and nitrogen and the lower moisture content, ash, fixed carbon, oxygen, and sulfur in biomass feedstock , the higher the bio-oil yield results [21, 22, 23].

Another biomass classification is based on the atomic ratio. It helps to estimate the heating value of a fuel, among other things. The lower oxygen-to-carbon (O/C) ratio, the higher the heating value of a biomass. On the contrary, when the hydrogen-to-carbon (H/C) ratio decreases, the effective heating value is reduced.

Atomic ratio of fuel decreases when its geological age increases, which means that the older the fuel, the higher its energy content results [1] as reported in the "van Krevelen diagram", Figure 2.1.

Unfortunately, among all the hydrocarbon fuels, the one produced from biomass results having the highest oxygen content. This is undesirable because oxygen has a negative effects on the on the heating value and stability of the produced bio-oil, as already said. On the contrary, high hydrogen content in the biomass results in high liquid yields. But, when there is oxygen in high percentage, it has the capacity to consume part of the hydrogen in the biomass, producing water, and thus the high H/C content is not translatable into high gas yield [1].

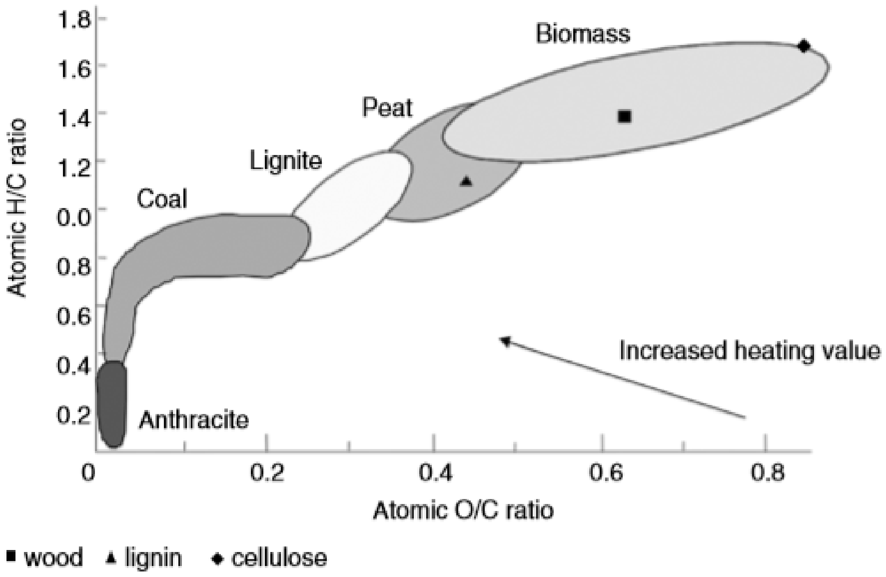


Figure 2.1: Van Krevelen diagram [1].

Correlation between oxygen-to-carbon (O/C) ratio and hydrogen-to-carbon (C/H) ratio on the bio-oil proprieties was recently studied by Xun Hua at al. [24]. The C/H ratio in the feedstock affects the elemental composition and the stability of the tar: the higher C/H ratio resulted in tar with higher stability, forming more aromatic rings of small size.

2.1.1 Wood Pellets

The pellets chosen for this research are shown in Figure 2.2, completely made with natural wood, certificated PEFC. Its diameter is 6 mm, and its length can vary from 0,5 to 2 cm.

Anyway, to evaluate as well the influence that the particle size of the biomass can exert on the final yield, the pellet has been also crushed and sieved in the range 1-2,5 mm.

Figure 2.2: Pellets asturias

The pellets has been selected because of its low content of ash, of metal as arsenic (As), lead (Pb) cadmium (Cd), chromium total (Cr), copper (Cu), nickel (Ni), mercury (Hg), zinc (Zn), of sulfur and chloride and its high LHV. The purpose is to use a material that can provide to a good liquid yield, making possible to compare the different bed materials, limiting any factor that could interfere with the activity level.

Pellets characterization

In order to evaluate the percentage of moisture, volatile matter, fixed carbon and ash in the wood pellet, TGA (Thermogravimetric Analysis) is performed, using a TGA Q500 V6.4 Build 193. Nitrogen is used to provide inert condition inside the furnace, setting a flow of 60 ml/min. First of all, amount of moisture is calculated by measuring the final mass lost after 30 min of isothermal condition at 105 °C (heating rate of 10 °C/min). Then, volatile matter is detected by measuring the mass lost at 900 °C kept for 5 min (heating rate of 10 °C/min). After that, the amount of ash is obtained by burning the remaining mass at 900 °C for other 5 min, substituting the nitrogen with oxygen. Finally, the furnace has been equilibrated at 40 °C. Instead, fixed carbon is evaluated by difference. The results obtained are shown in Figure 2.3.

High heating value (HHV) is mesured as well, using a bomb calorimeter of Mahler, resulting to be 18,88 MJ/kg. Results are summarized in Table 2.1.

2.1.2 Sewage sludge

Sewage sludge (SS) is a retained filter cake made by dewatering the solids remained in an effluent treatment plants [25]. SS is an unavoidable sub-product of the wastewater treatment process, it is generated in the form of very diluted suspension during primary (physical and/or chemical), secondary (biological) and tertiary treatments [26]. In the recent years has been registered a constant increase of the sewage sludge produced. This can become a serious problem since the disposal area are limited. That is why would become very useful

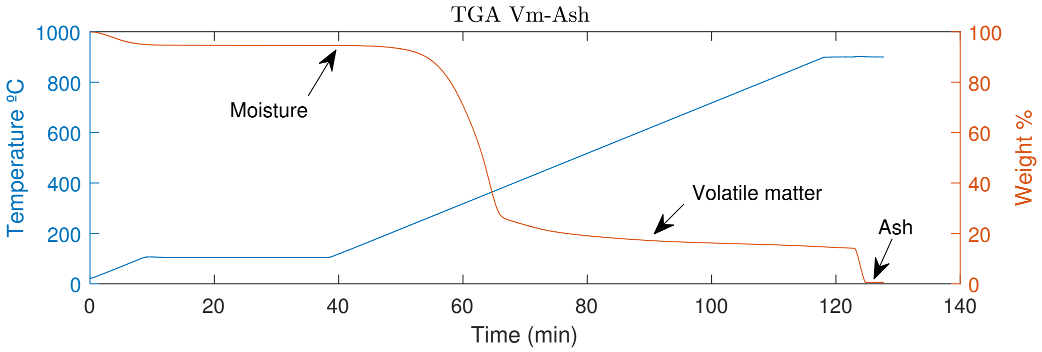


Figure 2.3: TGA curve

Table 2.1: Results of Proximate analysis (given results are wet basis) and Ultimate analysis of pellets.

Proximate analysis			
moisture [wt.%]	volatile [wt.%]	fixed carbon [wt.%]	ash [wt.%]
4,75	80,21	19,22	0,61
Ultimate analysis			
C [%daf]	H [% daf]	N[% daf]	O [% daf]
50,77	5,9	0,2	43,0

to find possible routes for its disposal. Valid alternatives to the agricultural utilization, which is no more acceptable, are the thermal treatments, such as combustion/ incineration, gasification, pyrolysis, hydrothermal treatment, wet air oxidation or supercritical wet oxidation [27]. Among these technologies, pyrolysis seems to be the best solution, considering the economic point of view. One of the main reasons supporting this conclusion is that pyrolysis is a zero waste method having a greater potential in the solution of the wastewater problem, and it is characterized by acceptable gas emission. Moreover, the biochar produced by SS pyrolysis, could be utilized for soil remediation, having positive effects on growing media microbial biomass. Even if in biochar there is a higher metal concentration than in SS, their transfer to plants seems to be reduced when compared with the direct disposal of SS.

Only recently, SS has been developed as a frontier research area if compared to the widespread application of its resource recovery techniques [28], so there are still several technological challenges. First of all, as already explained, biomass composition affects pyrolysis product. Studies have pointed out that for SS, low ash and high volatile contents are desired characteristics, enhancing liquid production [3]. Composition and properties of sewage sludge are variable, and they depend on several factors:

- the origin of the wastewater;
- methods used to treat the wastewater;
- environmental legislation;

- water reclamation requirements;
- seasonal variations;
- the duration and conditions of storage.

Liquid yield is one of the parameter that can be mostly affected by the sludge composition: the presence of potassium, lithium and calcium cations seems to reduce liquid yields [29]. More over has been found by Fonts et al. [30] that low ash and high volatile contents enhances liquid production. Bridle et al. [31, 32] discovered that primary sludge is better for the bio-oil production, than the secondary and the digested one. According to Font et al. [3], the SS liquid yield is in the range of 27-54 wt% on sewage sludge fed basis or 51-80 wt% on dry ash free (daf) basis.

The real challenging issue is represented by the high contents of oxygen, nitrogen, and sulfur in the derived bio-oil obtained by the pyrolysis of the sewage sludge, as reported by Fonts et al. [30], which must be removed from the final product if it is to serve as transportation fuel.

Sludge characterization

The sludge used has been taken by a waste urban water treatment plant of the south of Madrid. Elementary and proximate analysys has been provided as well as the measurement of the heat value. Obtained results are reported in Table 2.2. The HHV is 13,77 [MJ/kg]. Staying at what reported in literature, particle size is a determinant parameter for the obtainment of high liquid yield [3]. So, particular attention has been given to its choice: the smaller the size, the higher the liquid yield, but particle smaller than 0,3 mm can lead to an increase of gas production [33]. More over, if particles are too small, there is the possibility that some of them can be carried out of the reactor by the carrying gas.

Table 2.2: Proximate analysis and Ultimate analysis (given results are wet basis)

Proximate analysis			
moisture [wt%]	volatile[wt%]	fixed carbon [wt%]	ash [wt%]
8,18	54,10	2,36	35,36
Ultimate analysis			
C [%daf]	H [% daf]	N[% daf]	O [% daf]
30,77	5,28	4,55	59,39

2.2 Bed materials

Catalytic pyrolysis, as already discussed in the paragraph dedicated to the upgrading processes, refers to the application of catalysts to the pyrolysis processes. In order to obtain a higher quantity and quality of targeted products. In this thesis, only catalysts belonging

Figure 2.4: Dryed and sieved sludge

to the "in-situ upgrading" group are going to be tested, considered more convenient.

In fact, condensation of pyrolysis vapour to obtain bio-oil and the subsequent evaporation of bio-oil for upgrading purposes is not thermally efficient. Thus, the introduction of catalysts into the pyrolysis process, before the condensation of the vapour, in order to induce vapour-phase catalytic reactions, is a worthwhile and promising route.

Catalysts, as mentioned before, are not used only to improve the yield, but also to qualify the bio oil proprieties. In fact, bio-fuels contain significant amounts of oxygenated compounds which account for relatively low heating values, low stability, high viscosity, low volatility and low pH. The introduction of catalysts into the transformation process, designed in a specific way to enhance de-oxygenation, cracking and reforming reactions, is a possible option for overcoming most of these issues [1].

Ideal catalyst must meet the following specification [35]:

- good activity and efficiency on tar conversion in environments that contain high concentrations of H_2, CO, CO_2, H_2O and temperatures between 600 and 900 °C;

- good activity for methane reforming reactions when the focus is the hydrogen production;

- good stability to coke deactivation and H2S poisoning;

- easy regeneration;

- good resistance to friction;

- commercial availability and low cost;

- no environmental toxicity.

2.2.1 Sand

Sand is the only inert bed material, and it has been included in this study as a term of comparison [36]. So, in future considerations, activity of each bed-materials will be subjected to comparison with sand. Actually, it is commonly used as bed material in fluidized bed reactors. Its main constituent is SiO_2 [37] and due to its high mineral hardness (on the Moh scale) and attrition resistance, the material is suitable for this type of applications [36]. It is not porous and the Total Surface Area is 0.4654 m^2/g.

Although sand is low cost and abundant, it is not the perfect material to apply for FBR pyrolysis. In fact, it is subject to the formation of agglomerates when used as bed material in a fluidized-bed reactor during biomass fast pyrolysis, interacting with the pyrolyzing biomass particles, attaching the active sites produced by the reaction [38], preventing the mixing in the bed or leading to defluidization [37, 39].

2.2.2 Sepiolite

Sepiolite is a fibrous, hydrated Mg-Al silicate clay mineral. Tetrahedral Al appears with a frequency of 0.4-0.48 atoms per twelve tetrahedral sites. The discontinuous octahedral sheets provide for infinite channels along the fibre axis. During crystal growth, a second set of irregularly shaped pores with a diameter of $\sim$ 100 Å is created within the fibre. The presence of channels and pores in the structure accounts for both the high surface area and the capacity to adsorb various materials [40].

The hysteresis resulting from the BET analysis (Figure 2.5) is evidence of mesoporosity. More over, staying at the IUPAC classification, it appears that the pore distribution is very narrow. The obtained data are reported in Table 2.3. Sepiolite, thanks to its structure, can be successfully applied for reactions, such as syntheses, polymerization, and thermal or chemical decomposition of organic molecules [41]. A. Veses et al. [42] have investigated on the influence that low cost catalysts (sepiolite, bentonite, attapulgite and red mud) can have on the pyrolysis of biomass in an auger reactor system. It was determined that the ratio of catalyst to biomass was critical to aim the pyrolysis for liquid production. Otherwise, a too high catalyst proportions seemed to maximize char production. Regarding the quality of the organic phase, it was observed that each material tested, reduce remarkably the viscosity of the obtained bio-oil, and improved its stability.

Table 2.3: BET analysis for sepiolite.

Micropore Volume [cm^3/g]	0,012
Micropore Area [m^2/g]	23,81
External Surface Area [m^2/g]	86,15
Total Surface Area [m^2/g]	109,96

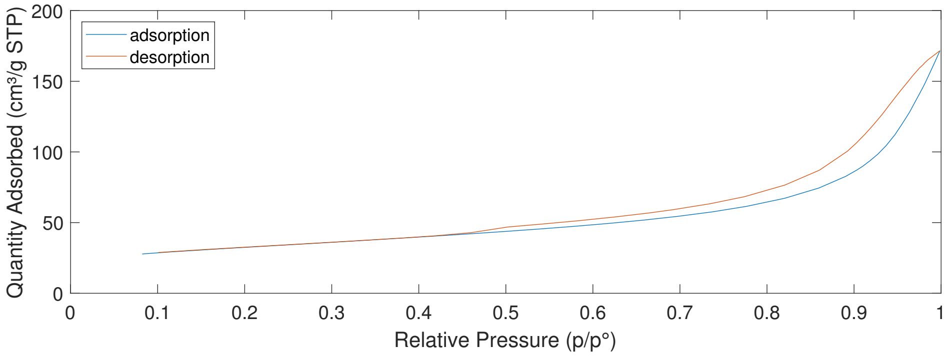


Figure 2.5: N_2 adsorption and desorption isotherms from the BET analysis on sepiolite.

2.2.3 Dolomite

Dolomite is a natural material and it is made of calcium and magnesium compounds, having as overall chemical formula $CaMg(CO_3)_2$, with 20 % of MgO, $\sim$ 30 % CaO, $\sim$ 45 % by weight of CO_2 and a small amount of mineral impurities. It is not a porous material, as demonstrated by the results obtained with the BET analysis (Table 2.4). Use of dolomite has obtained a great attention for various processes. Due to its basic nature, it is known as a useful catalyst for biomass gasification at high temperature, having the capacity to reduce tar formation by cracking volatile vapor, reforming high molecular weight compounds, and enhancing yield and quality of the syngas. Dolomite has also showed the capacity to improve the bio-oil quality. Catalytic cracking converts heavier organic matters to lighter fractions, and removes oxygen from oxygenates compounds [43]. In the study carried out by Hoang Vu Ly et al. [43], is reported that the use of Dolomite for tulip tree (Liriodendron) pyrolysis in FBR, can make the yield decrease, if compared with the one obtained using sand: it passes from 49.03 wt% to 44.83 wt%, but obtained bio-oil presents a higher HHV, and a lower content of oxygen. When it has been used for catalytic upgrading, as reported in the research of Valle et al. [44], the resulting bio-oil presented an effective reduction in O/C ratio, carboxylic acids and sugars (mainly levoglucosan). In the research conducted by Conesa and Domene [45] on the pyrolysis of the Posidonia oceanica in presence of dolomita, it is shown that this catalyst can limit the tar production, increasing the yield of bio-oil. Similar results have been obtained by Tursunov [46], who has compared dolomite and zeolite in a fixed bed reactor used for the pyrolysis of carboxylic acids and sugars (mainly levoglucosan): dolomite resulted a better catalyst in the improvement of gas yield, at the expense of char.

Table 2.4: BET analysis for dolomite.

External Surface Area [m^2/g]	0.6842
Total Surface Area [m^2/g]	0.5687

By the way, dolomite exhibits a decrease in the mechanical strength over time, and it is more evident in fluidized beds. However, once that the activity is significantly reduced, the catalysts can be replaced without great expenses. Deactivation due to carbon deposition is another highlights. Dolomite is very subject to this phenomenon but has been pointed out that a relatively high amounts of steam is effective in maintaining these catalysts active, by reforming deposited carbon [47].

2.2.4 Alumina

PURALOX is a high-quality aluminium oxides fabricated via the controlled activation of Sasol's alumina hydrates, PURAL and CATAPAL [48]. It is available as white free flowing powders with high-purity, providing excellent specific catalytic activity, high surface area, stability, and low attrition loss. BET analysis conducted on this material are reported in Table 2.5. It appears that the material is mesoporous, and by the comparison of the adsorption curve (Figure 2.6) hysteresis is observed with a shape that would indicate the presence of pores in a very narrow range (IUPAC classification). Due to its high thermal stability, PURALOX is widely used for washcoat formulations in environmental emission-control catalysts. Furthermore, recent developments have found other suitable uses for these materials in applications outside catalysis area, such as polishing, chromatography, adsorbents and gas separation. Thanks to its high level of attrition resistance it is often used in fluid bed applications.

Table 2.5: BET analysis for alumina.

Micropore Volume [cm^3/g]	0.002538
Micropore Area [m^2/g]	5.77
External Surface Area [m^2/g]	142.76
Total Surface Area (BET) [m^2/g]	148.53

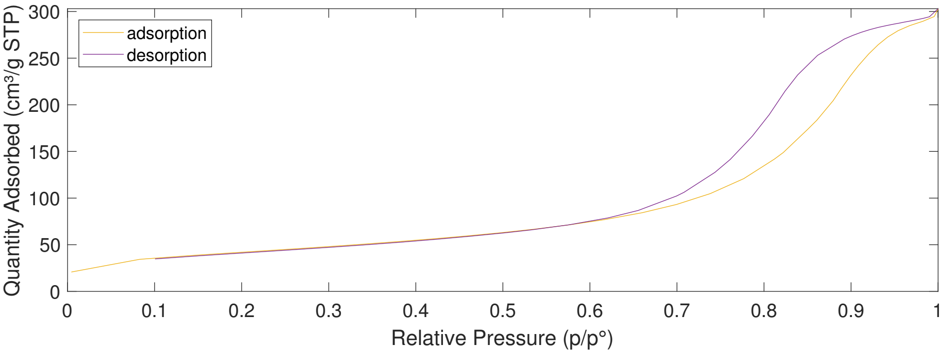


Figure 2.6: N_2 adsorption and desorption isotherms from the BET analysis on alumina.

Matsuoka et al. [49] have reported that alumina catalyst can be used to decrease the amount of tar formed in the gasification of wood chips at 500-700 °C. Tar captured in the alumina can be subsequently reformed with steam to give synthesis gas. Yourgun and Simsek [50] studied the effect of alumina to the miscanthus grass pyrolysis. They showed that the content of aliphatic and aromatic hydrocarbons was increased as compared with non-catalytic pyrolysis, obtaining also high liquid yield. However, further analysis has pointed out that bio-oil formed was highly dominated by oxygenated species. Catalytic effect of metal oxides (Al_2O_3,CaO,Fe_2O_3, TiO_2,and ZnO) on pyrolysis of sewage sludge was investigated by Shao et al. [51]. They found that Al_2O_3 promotes degradation of organic matters, with in the whole pyrolysis temperature range. Aysu et al. [52] investigated the pyrolysis of liquorice stalks (Glycyrrhiza glabra L.) which was performed in a fixed-bed tubular reactor with (ZnO, $FeCl_3$, K_2CO_3, Al_2O_3, $Na_2B_4O_7 \cdot 10H_2O$) and without catalyst at three different temperatures (350,450, 550 °C). According to them, alumina has reported the highest bio-gas yield, and the lowest production of bio-char, compared with the other materials used. In the studies supported by Shadangi et al. [53], thermal and catalytic pyrolysis of Karanja seed has been compared, using different bed materials (CaO, Al_2O_3 and kaolin). They confirmed that catalyst had an effect on the yield of liquid, reporting a marginal increase (2-3 %) for Al_2O_3 and kaolin catalytic pyrolysis compared with thermal pyrolysis. The effects on the bio-oil proprieties, obtained in presence of the catalyst are more interesting: pH and HHV increased while viscosity decreased. A similar result was also found by Azuara et al. [54], but experimental study was focused on sewage sludge pyrolysis in a Fluidised Bed Reactor, and the purpose was the comparison of sand and γ alumina as bed material. Stefanidis et al. [55] investigated on the in-situ catalytic upgrading of biomass fast pyrolysis, using several bed material, and comparing them with the silica sand. It was shown that, the presence of whatever catalyst used (alumina included) made gas yield increased, and liquid and solid yield decrease. More over, alumina was effective in reducing ketones and heavy compounds concentration, providing a bio-oil with better stability. It was also the most selective towards aromatic hydrocarbons production and exhibited the best bio-oil quality for fuels production. Furthermore, it obtained a reduction in oxygenated compounds, taking in account that the organic fraction produced by thermal pyrolysis was highly oxygenated (41.68 %oxygen content). The same result was found by Kaewpengkrow et al. [56], researching on catalytic upgrading of the pyrolytic vapors after fast pyrolysis. Moreover, they have shown that Al_2O_3 catalysts seemed to promote N-compounds.

2.2.5 Olivine

Olivine [$(Mg,Fe)_2SiO_4$] is a silicate tetrahedral mineral in which is possible to find magnesium and iron cations [57]. It results to be active for the tar reforming, thanks to magnesite (MgO) and iron oxide (Fe_2O_3), created during calcination of the material. As primary catalyst, it has the function to promote reactions as water gas shift and steam reforming, minimizing tars and increasing both hydrogen and CO_2 production [58]. Even if olivine is highly resistant to the attrition, it is subjected to deactivation phenomena due to coke formation, which covers active sites [59]. Anyway, being a low cost material, it is easy to replace.

Several studies has tested olivine for in situ catalyst applications. Donghoon et al. [60] has demonstrated that olivine has the propriety of increase gas and liquid yield produced by biomass (lignin) pyrolysis at the expenses of char and coke. Sujing et al. [61] compared olivine with alumina, in a fluidized bed reactor, reaching the conclusion that olivine is more reactive, obtaining the same yield of alumina, but at lower temperature. Moreover, it can give a better quality oil, with lower oxygenated compounds and higher HHV. Instead, Corella et al. [59] compared the performance of olivine with the one of dolomite, in a fluidized bed rector, pointing out that dolomite is 1,4 times more reactive than olivine for tar reduction. Tuomi et al. [62] have investigated on the role played by the pressure, discovering that gas yield can increase at the tar expenses, if the pressure is risen up (the study has been provided in the range 0-10 bar), contrarily to dolomite and MgO, which act in the opposite way.

2.2.6 Ni based catalyst

Ni based catalyst results very adaptable for fluidized bed reactor due to its high mechanical resistance and chemical and physical stability [63]. It has been mainly used for volatile reforming, in order to enhance H_2 and CO_2 production. It demonstrates high activity for the steam reforming of different feeds derived from pyrolysis of biomass and plastics [64]. In fact, staying at what reported by a recent review [65] the Ni/Al_2O_3 catalyst promotes several important chemical reactions such as water gas shift and steam reforming. So, it can offer the possibility to increase the gas production at the expense of tar. A method to increase the bio-oil yield has been also studied [8]. One of these researches, as reported in a review of 2008 [14], has been conducted on the Euphorbia rigida that is pyrolysed in presence of steam, founding that bio-oil yield increases from 21.7 wt.% (without catalyst) to 38.6 wt.%, adding 10 wt.% of catalyst. More over, the oil produced was containing fewer amounts of oxygen content with a higher H/C ratio than the original feed stock and very similar to the one of light petroleum products (H/C = 1.5–1.9). However, there are some challenges in Ni-based catalysts utilization, such as fast deactivation due to carbon deposition on the catalyst surface or strong tendency to create agglomerations [66].

Catalyst preparation

Nickel based catalysts was prepared by incipient impregnation technique with 10 wt% of metal. Calculated amount of metal nitrate $Ni(NO_3)_2 \cdot 6H_2O$ (99.99%), was dissolved in deionized water and added to the Al_2O_3 support drop-wise with constant stirring. Then, the sample was dried in oven at 105 °C overnight before calcination at 600 °C for 3 h. Finally, in order to obtain the same particle size of the others bed materials, it was sieved in the range 280-425 µm (Figure 2.7).

2.2.7 Bio-char

Bio-char has gained the attention of several studies [9], because of its attractiveness as a low cost catalyst originates directly inside the gasifier through natural production. Most of them are focused on wood bio-char, which leads to the formation of further gaseous

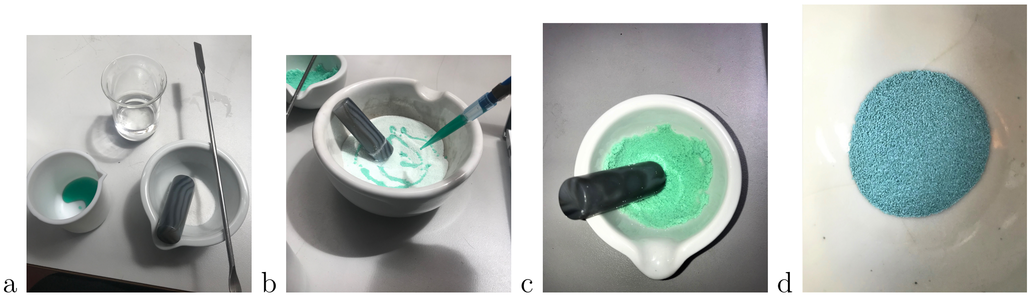


Figure 2.7: Catalyst preparation: (a) preparation of the material for the incipient impregnation,(b) Ni solution is dripped on the alumina, using a pipette, (c) once that Ni solution ends, alumina appears homogeneous, and it is ready to be dried up, (d) after the dried up and the calcination, the color of the alumina has changed tonality.

components from primary wood-tar cracking [67]. Same results has been found by Bridgwater et al. [68] who has studied bio-char reactivity at different temperatures. El Rub et al. [69] and Gilbert et al.[70] have also compared its catalytic activity with other catalysts used conventionally for tar reduction. In particular, it is found out that it gives moderate phenol conversion, and a very high concentration of CO and H_2, reacting itself with reactive gasses, so it results to be consumed over time, but it is not a big deal considering that it is continuously generated. In general, it is concluded that it might be a very promising material for solving the tar utilization problems in gasication systems: pore structure of char particle and mineral content can play a peculiar role for this achievement.

2.3 Minimum fluidization velocity

Considering that interactions between particles can be differents, depending on the material, the minimum fluidization velocity is estimated, for each one, employing the correlation of Carman-Kozeny (eq. 2.1):

$$U_{mf} = \frac{(\phi d_{bm})^2(\rho_{bm} - \rho_g)}{180\mu_g}\frac{\epsilon^3}{1-\epsilon} \tag{2.1}$$

where:

- g is gravitational acceleration;
- ϵ is void fraction of the dense phase particles;
- ρ_{bm}, ϕ, and d_{bm} are density, sphericity, and diameter of the bed material particles;
- ρ_g and ν_g are density and dynamic viscosity of the fluidization gas.

Particle size distribution curve has been traced for each material and for the operation, sieves of 106 μ m, 180 μm, 250μm, 425μm, 600μm have been used. Obtaining the curves reported in Figure 2.8. In order to maintain a certain comparability among the results

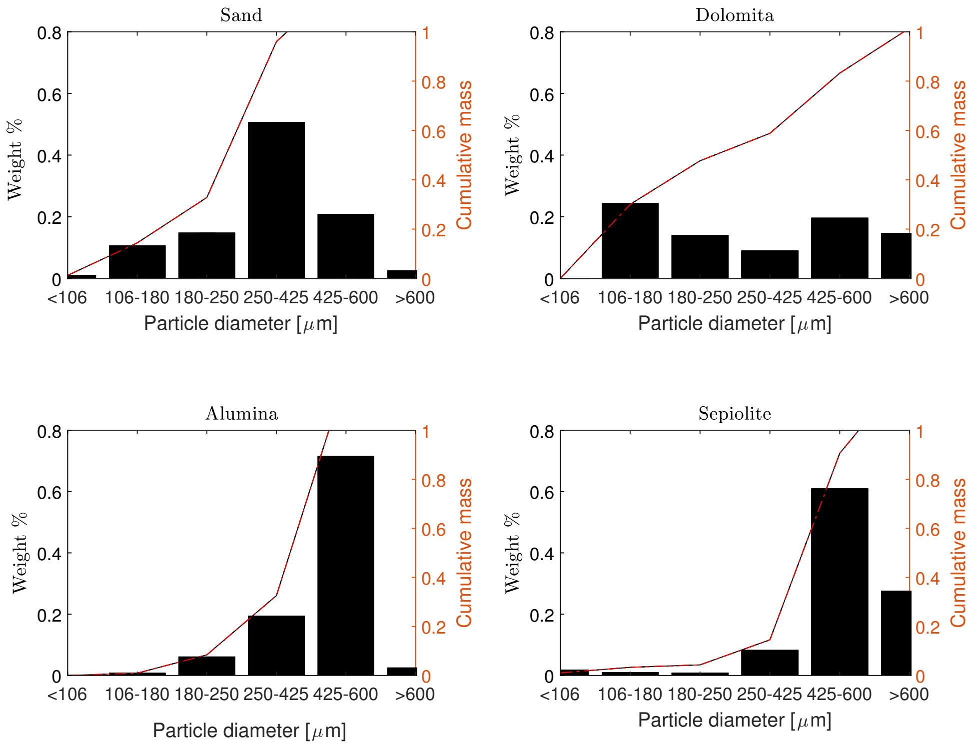


Figure 2.8: Particle size distribution for the bed materials.

obtained with the different materials, sieving operation has been provided, collecting particles belonging only to a small size range. With this strategy has been avoided that other factors, linked with the size of the particles, could affect the results. So, before the evaluation of bulk density, apparent density and porosity as reported in Table 2.6, materials have been sieved in the range 425-250 μm. According to Geldart's classification, this dimension belongs to the type B: solids sand-like. These solids are well fluidized with a vigorous bubbling action and are characterized by bubbles that grow large. For each material is

Table 2.6: Bed material proprieties.

	sand	sepiolite	dolomita	alumina	olivina
apparent density $[kg/m^3]$	2583,83	1487,50	2629,37	1484,48	3102,62
bulk density $[kg/m^3]$	1552,14	749,40	1505,29	816,74	1707,98

calculated the mass necessary to obtain the fixed-bed height (h_b) equal to 5 cm, corresponding to bed aspect ratio (h_b/d_i) of 1, as it is shown in Table 2.7. Entertainment of bed material particles is prevented by using a reactor height 10 times longer than the one of the fixed-bed. Further more, to avoid this problem, the particle size has been chosen properly (removing the finest size).

Table 2.7: Values of the bed materials mass to use in the FBR.

	sand	sepiolite	dolomita	alumina	olivina
mass [g]	152,30	73,53	147,70	80,14	167,6

For the estimation of the minimum fludization velocity, its dependence on temperature has been taken in account. Both density and dynamic viscosity of the carrier gas change considerably with temperature. Their values are evaluated by interpolation of the data furnished by the engineeringtoolbox. Nitrogen was assumed an ideal gas, as proposed by Sanchez-Prieto et al.

To evaluate the validity of the correlation of Carman-Kozeny, an empirical measurement has been provided as well. It was performed by visual inspection of the bed surface, detecting the presence of bubbles, each 50 °C, as reported by Soria-Verdugo et al. [72]. In fact, according to Geldart's classification, particles type B have a special characteristic: the minimum bubbling velocity is coincident with the minimum fluidization velocity. Measurement is conducted by reducing the values of the gas flow rate, from vigorous bubbling fluidized bed up to fixed bed stage. This method is adopted to prevent that the cohesive forces between particles could affect the results.

Comparing the collected data and the theoretical ones, high accuracy of the Carman-Kozeny correlation is demonstrated (Figure 2.9). As expected, increasing the temperature a decrease of U_{mf} is registered, for all the materials.

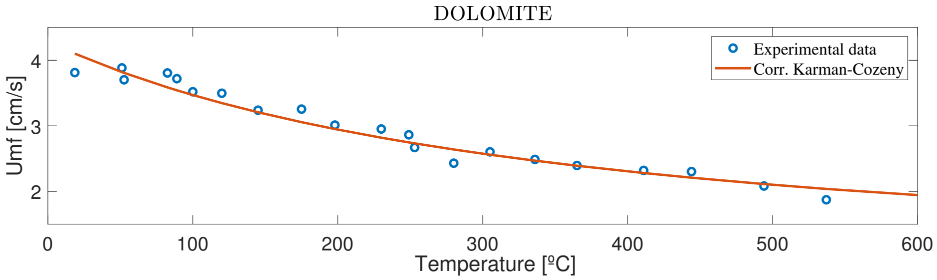


Figure 2.9: Minimum fluidization velocity: Theoretical vs. experimental values.

2.4 Deactivation phenomena

The main drawbacks of catalytic processes are the cost and the deactivation of the catalysts. So, it is important to be aware on the resistance that the bed material offer to this phenomena. Phenomena of deactivation of the catalyst, during biomass fast pyrolysis, has already been studied, but mainly for commercial catalyst as ZSM-5. Instead, for the other bed materials there is a lack of information.

As reported by Kalogiannis et al. [75], who studied the deactivation of the natural MgO catalysts (basic), four type of catalyst deactivation are detected:

Coking and blockage of catalyst pores , related to the decomposition of the oxygenates compounds and the re-polymerization of phenolic oxygenates [76]. It is easily recoverable by burning off the coke.

Hydro-thermal deactivation witch is caused due to contact with water vapor at high temperature. It causes the increase of coke and char production, resulting in further losses of the activity. The water vapor can derived not only from the moisture, presents in the biomass, but even from dehydration that take place during the reaction itself.

Poisoning from biomass alkali metals such as K, Na, Mg and Ca that are commonly found in biomass. As residual ash are deposited on the acid sites of the catalyst, rendering it inactive and less selective. By the way, this type of deactivation seems to affect only catalysts with acid nature, and not the basic ones. However, this phenomenon results unrecoverable.

Sintering effect caused by the high temperature used.

Chapter 3

Experimental setup and methodology

3.1 Lab-scale FBR

The pyrolysis experiments were conducted in a cylindrical reactor made of stainless steel, with an inner diameter (d_i) of 4.7 cm and a height (h) of 50 cm, operating at atmospheric pressure.

The energy required to reach the desired temperature was supplied by three electric resistors, surrounding the reactor and capable of supplying maximum thermal power of 1.2 kW_t. Nitrogen is used as fluidizating agent, providing to the required environment, oxygen free. The nitrogen flow rate was controlled by a flow regulator and measured by a digital flowmeter PFM710-C6-E from SMC, with a measurement range between 0,2 and 10 l/min.

The reactor was placed on a precision scale PS 6000 R2 from RADWAG. The weight measurements, conducted during the pyrolysis tests, were below the maximum weighting requirement of the scale for all the cases analyzed. Furthermore, the accuracy of the device, always met the requirements of the experiment. Figure 3.1 shows a schematic of the facility.

The reactor temperature was measured by a type-K thermocouple immersed in the bed and connected to a recorder. Once the desired temperature was attained, recorder was started up, and flow rate of nitrogen was adjusted to the specific value. Then, the pyrolysis occurred and the vapor released, was absorbed by a fume extractor placed above the reactor.

3.2 Materials preparation

Before that the experiment is performed, both wood pellets and sewage sludge are sieved in the range of particle diameter 1-2.5 mm, and subsequently, they are dried up at 105 °C for three hours in a universal oven UFE 500 from Memmert. After that procedure, the

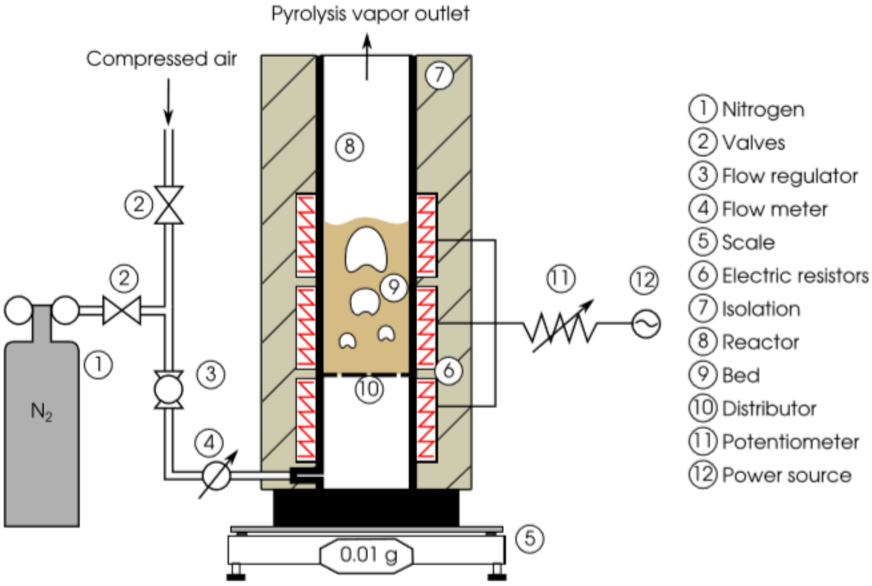


Figure 3.1: Schematic of the experimental facility [72].

biomass is divided in samples of 10g each and stocked in cups collocated in a dryer filled with silica gel. Samples remain in the dryer until the moment of their utilization, in order to avoid that air humidity could be adsorbed by the porosity of the material. They are removed from the equipment just before that pyrolysis starts, remaining in contact with the atmosphere only few seconds.

Bed materials, do not required particular procedure for their preparation: they are only sieved, as previously said, in the range 250-425 μm and weighed.

For what concern the reactor, it is cleaned after every cycle, with the scope of removing all the tar deposited on the lateral surface. This operation should be done properly, otherwise the fluidized bed particles and the pieces of biomass, might remain attached on it. For the same purpose, the thermocouple too is cleaned after every cycle.

3.3 The excess gas velocity

Before the experiment, the excess gas velocity to use for each bed material is calculated. In fact, as reported in literature [68, 77], the excess gas velocity causes an increase of the total volatile matter released, and it may be attributed to the higher heating rates of the fuel particles, obtained due to the higher convection coefficients and axial mixing rates. However, it is necessary to take into account that a too high gas velocity may cause the entertainment of the bed material during the experiment, registering a false weight loss. So, it has been necessary to find a good compromise, selecting a U sufficiently higher than the gas velocity of the minimum fluidization U_{mf} previously found, but not too much.

$$d = U - U_{mf} > 0 \tag{3.1}$$

In order to have the same conditions for all the materials, the difference between the two velocities is fixed at d = 9,11, remaining in the range suggested by Morato et al. [16], promoting a vigorous bubbling regime. Then, considering the section of the reactor (S_{reac}) and the temperature at which the experiment has been performed (T_{pyr}), gas volume flow ($\dot{V}$) has been calculated for each material, as reported in Table 3.1.

$$U = U_{mf} + d \tag{3.2}$$

$$\dot{m}(T_{pyr}) = U S_{reac} \rho_{air}(T_{pyr}) \tag{3.3}$$

$$\dot{V}(T_{amb}) = \frac{\dot{m}(T_{pyr})}{\rho_{air}(T_{amb})} \tag{3.4}$$

Table 3.1: Gas velocity, ratio U/U_{mf} and volumetric flow rate calculated for each bed materials.

	sand	sepiolite	dolomita	alumina	olivina
U [cm/s]	12,15	11,19	11,13	10,76	14,90
ratio U/U_{mf}	4	5,18	5,52	6,53	2,57
$\dot{V}$ [l/min]	5,11	4,73	4,68	4,53	6,27

3.4 Signal Analysis

From the described equipment, two type of signals are provided: temperature profile and weight loss curve. The mass signal gives the quantity of total mass loss caused by the volatilization of bio-oil and gas. It is measured by the scale during the experiments and it is affected by the vibrations induced by the bubbles regime. Therefore, it is filtered using a moving average, as reported in [72]. The filtered signals were proved to follow the average behavior of the raw signal measured by the scale in all cases as illustrated in Figure 3.2.

$$\left(\frac{dm}{dt}\right)_{vol} = \left(\frac{dm}{dt}\right)_{gas} + \left(\frac{dm}{dt}\right)_{bio-oil} \tag{3.5}$$

Once that the signal is filtrated, it is used to calculate the yield of the volatile released, to plot the conversion curve and its derivative, and to make some more consideration about the kinetic of the reaction, such as the kinetic constant and the time of pyrolysis, t_{pyr}.

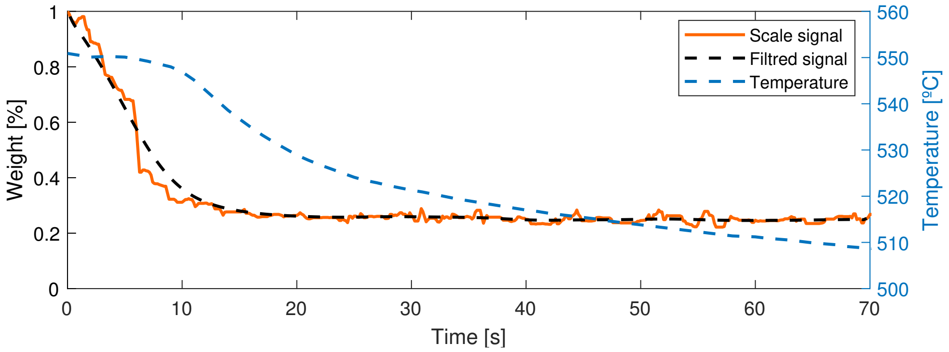


Figure 3.2: Pellets pyrolysis.Bed-material: sand (upper left), alumina (bottom left), sepiolite (bottom right), dolomita(upper right).

3.4.1 Pyrolysis Kinetic model

Pyrolysis consists of a huge number of parallel and consecutive reactions, which are in competition to each other. That makes very difficult to get a model which considers the evolution of each reagents and/or products. For this reason, it is necessary to use a simplified approach [74]. In the literature, two kinds of model are mainly used: one-component model, which takes in account only the biomass decomposition; and the three component model which, instead, considers that biomass is composed by pseudo-components cellulose, hemicellulose and lignin.

In this work, the one-component model is adopt because the purpose of the thesis is to compare the devolatilization kinetics in total, between SS and wood pellets, and not finding any reaction schemes. It resulted to be sufficiently accurate [74].

$$\frac{dm}{dt} = -km_{vol}(t)^n \tag{3.6}$$

where $m_{vol}(t)$ represents the mass of the volatile content of the biomass at the time t, k is the apparent kinetic constant and n is the order of the reaction.

$$m_{vol}(t) = m(t) - m_{char+ash} \tag{3.7}$$

With this approach, the order of the single reaction is replaced with a global reaction order, which can be evaluated as follow, using the following integrated equations:

- First order of reaction

$$ln(m_{vol,0}) - ln(m_{vol}(t)) = kt \tag{3.8}$$

- Other order of reaction

$$\frac{1}{n1}\left(\frac{1}{m_{vol}(t)^{n-1}} - \frac{1}{m_{vol,0}^{n-1}}\right) = kt \tag{3.9}$$

In literature it is very common to use the first one, but in the cases in which it was considered inaccurate, the 1.5 or the 2 order have been adopted as well.

The k can be calculated by the regression of the Eq. 3.8, or the Eq. 3.9, and its approximation can be evaluated due to the correlation coefficient, R^2

Considering that the model should not contain any information about the transport phenomena or the secondary reaction occurring, the obtained apparent kinetics can be utilized to reformulate the Eq 3.8 or the Eq 3.9, applying the simple exponential model, based on the conversion of the mass. To determine the mass loss of volatile, using a first order, the equation become:

$$m_{vol}(t) = m_{vol,0}e^{-kt} \tag{3.10}$$

which can be rewrite in the following way to be comparable with the balance signal:

$$m(t) = (m_0 - m_{vol,0}) + m_{vol}e^{-kt} \tag{3.11}$$

For each catalytic material, the apparent kinetics, describing the conversion of the biomass in the FBR, is calculated and compared.

Yield measurement

The yield is calculated using the following equation, which takes in account the mass of volatile compounds released m_{vol} over the total mass of biomass introduced in the reactor m_0:

$$Yield = \frac{m_0 - m_{fin}}{m_0} \tag{3.12}$$

The end of the pyrolysis process (t_{fin}) is considered to occur when the derivative of the mass is less than 0.5 %:

$$m_{fin} = m(t_{fin}) \tag{3.13}$$

$$\left(\frac{dm}{dt}\right)_{t_{fin}} = 0{,}0005 \tag{3.14}$$

Pyrolysis reactivity measurement

The method used to compare the different behaviors of the reactions in the different cases, has been obtained form Fischer et al. [78], in which it is used for the gasification of bio-char.

$$r_{vol} = \frac{d\chi}{dt} \tag{3.15}$$

$$\chi = \frac{m_0 - m(t)}{m(t_{fin})} \tag{3.16}$$

where:

- r_{vol} is the reactivity of the biomass,
- χ is the conversion of the biomass in volatile compounds,
- m_0 is the initial mass of the biomass, equal to 10 g,
- m(t) is the instantaneous remaining mass.

The pyrolysis time, t_{pyr}, is also checked. It can be estimated as the time needed to reach a determined value of the reacted fraction. In this work, a value of χ= 95 % is selected to determine the pyrolysis time according to Soria-Verdugo et al. [72].

Temperature profile

Thanks to the thermocouple collocated in the fluidized bed, it is possible to record the temperature during the carrying out of the reaction. From the data obtained, the profile of the temperature derivative is also plotted.

The reaction results endothermic, in almost all the cases, reporting a negative slope, but it is necessary to take in account that in some particular cases, it has some exothermic behavior as well, involving a positive derivative too.

To make some more consideration about the temperature trend, three new parameters are introduced, trying to take in account both possibilities (exothermic and endothermic reactions):

- $y_{min} = \frac{dT}{dt}_{min}$ is the minimum value of the slope of the temperature profile, representing the point where the temperature decreases more rapidly. It is caused by the endothermic nature of reaction occurring, and consequently it is negative.
- $y_{cooling} = \left|\frac{dT}{dt}\right|_{min}$ is the minimum point of the absolute value of the slope of the temperature profile, representing the speed of the cooling down of the reactor when no reaction occurs.
- $y_{max} = \frac{dT}{dt}_{max}$ is the maximum value of slope of the temperature profile, representing the speed of the heating up when exothermic reactions occur. It is the only case in which the slope is positive.

3.5 First experiment: comparison among bed materials

The first experiment consists in recording the mass signal registered by the precision scale, on which the reactor rests while the pyrolysis of biomass occurs. The experimental process was composed of three stages:

Attainment of desired pyrolysis temperature: the first stage is the heating up of the reactor. Air is used as fluidization agent and three electric resistors supply to thermal power until the desired temperature is reached. To have enough time to performed all the successive operations, a temperature of 20ºC higher than the one desired for the pyrolysis experiment need to be reached.

Biomass conversion due pyrolysis: once the desired temperature is attained, gas flow is switched to Nitrogen and its flow rate is adjusted to the specific excess gas velocity, previously calculated. After that,the resistances are disconnected from the electricity and the scale is tared. So, the recording of the weight starts and a mass of around 10 g of dried biomass, is introduced from the top of the reactor in a batch.

Reactor cool down: when the weight become stable, the recording is stopped and the reactor is left to cool down, using the N2 as fluidizing agent. Only once that the temperature is sufficiently low to avoid any combustion, caused by the external O2, the bed material, together with the biochar formed, are removed and sent to further analysis. The pyrolysis experiments were replicated 4 times for each bed materials tested, to check the repeatability of the experimental procedure, attaining deviations lower than 5% in all cases.

Biochar analysis

The bio-char, collected from the previous experiment, is carefully sieved and analyzed. Analysis considered important to compare the different cases are the BET, the measurement of the HHV (Higher Heating Value) and the CHNO, to determine if the mineral exercises any effects on the char structure or composition.

BET: the analysis has been performed with TriStar II 3020 V1.03 using N_2 as analysis adsorptive, particularly suggested for mesoporous material. Before starting the test, degas is provided, keeping the sample for two hours at 200 °C, while the test itself has been kept running overnight. Both External Surface Area and Total Surface Area (BET) have been measured.

Calorimetry: the HHV of the bio-char has been measured with a bomb calorimeter of Mahler. Because of the dusty nature of the char, to perform the analysis, a previous compaction of the sample into pellets has been strictly necessary, using pressure of 150 bar.

3.6 Second experiment: char deposition

To study the effects caused by the char deposition on the surface of the catalyst, a cycle has been performed. It consists in repeating several times the previous experiment described, using always the same bed material, instead of a fresh one. Between one repetition and the other, the cooled material is sieved in order to remove the big particles of bio-char formed. After each cycle, a certain amount of bed-material get lost, because of the sieving operation, the formation of aggregate with the char etc. So, to maintain it constant during the whole experiment, it was feed up by adding to the principal cycle the missing quantity of bed material, taking it from a secondary cycle, carried out in parallel. It is important to specify that N_2 is used for both, cool down and warming up, to avoid any possibility of regeneration and char combustion.

To see the transformation in the bed material appearance due to the phenomena of char deposition, a series of photos are taken during the cycle, reporting the color change.

3.7 Third experiment: phenomena of deactivation due to ash deposition and regeneration

When the reactor is heated up with air (considering that temperature reaches values up to 570 °C), combustion could take place inside the reactor, so, if there is some char deposited on the bed materials from the previous pyrolysis, it burns up forming ash. This ash can easily cover the active sites, provoking a phenomenon of deactivation of the material.

In order to check its evolution, a cycle has been performed, heating up the reactor with air, and cooling down with N_2. The only bed materials subjected to this experiment are sand and dolomite. Obtained yields and weight-loss curves are compared with the ones obtained from the second experiment.

As in the previous cycle, between one repetition and the other, the cooled bed material is sieved and re-collocated in the reactor.

Only for the dolomite, showing an important deactivation, a complete regeneration is provided, in correspondence of the 10^{th} repetition, keeping the material in a furnace at 650 °C for two hours. After this procedure, the cycle is continued for other 4 repetitions, detecting the effects of the thermal treatment.

To check the effectiveness of the active sites covering, would be interesting to perform on the minerals a TPR analysis, before and after the experiment. But, because of shortage of time and proper equipment, it is not provided in this work.

3.8 Fourth experiment: accumulation of bio-char

A cycle of five repetitions is performed to study the effect of the bio-char accumulation in the fluidized bed reactor and its possible attitude as catalyst. Both, wood pellets and sludge, are tested in this experiment, with the aim to detect possible differences between the two deriving bio-char.

Differently from the second experiment, once that the bio-char is formed, it is not removed by any sieving operation. After that the first pyrolysis is performed, the reactor is directly warmed up again, until that the desired temperature is reached, continuing to perform the successive repetition, accumulating, cycle by cycle, the bio-char in the fluidized bed. It is important to underline that, as in the second cycle, only the N_2 is used as fluidizing agent, to avoid any combustion of the formed byproduct.

Chapter 4

Results and Discussion

4.1 First experiment: effects caused by the use of the bed materials

In the first experiment, pellets and sludge pyrolysis is performed using five different bed materials, such as sand, sepiolite, dolomite, olivine and alumina. The purpose of the experiment is to compare the effects linked with the biomass and the catalysts nature, analyzing both the weight loss and the temperature trend.

The resulting yields are observed in Figure 4.1, where it is possible to see that for wood pellets, dolomite achieved the highest conversion (80 wt.%), while sepiolite and sand, seem to be the worst materials, providing the lowest yield (72 wt%). Olivine produced a yield of 77 wt.% and alumina 74 wt.%. Looking at the results obtained with the sludge, the yield resulted much lower than the previous case. This is in agreement with the proximate analysis of both wood and sludge. In general, bed materials seem to keep the same order in providing their catalytic performances: dolomite results again the best material, with the highest yield (52,5 wt.%), followed by olivine with a yield of 47 wt.%. Sand displayed the worst performance (yield of 43,1 wt.%), though very close to the one obtained using alumina (44,7 wt.%) and sepiolite (44,6 wt.%). Figures 4.2 and 4.3 shows the results for

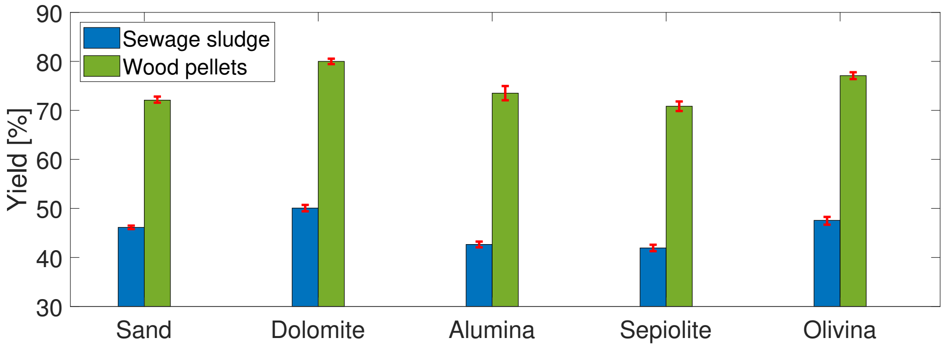


Figure 4.1: Yield comparison among all the considered cases

the reactivity. In the case of wood pellets, quite all the reaction rates have a point of maximum, demonstrating the presence of a point of flex in the conversion. In these cases, the first order model is less accurate, and to make it fit we have to neglect the beginning of the reaction, as can be ascertained by the Figure 4.4. However, for alumina, the conversion curve has no point of flex and its kinetic can be easily approximate with the proposed model. The situation changes completely when sewage sludge is pyrolysed, showing a point of flex only for the conversion obtained with olivine. It is the only material showing a bad approximation with the first order model, while it works properly for all the others. In general, the model fits better for the SS than for the wood pellets, as showed by the value of the standard deviation in the Table 4.1.

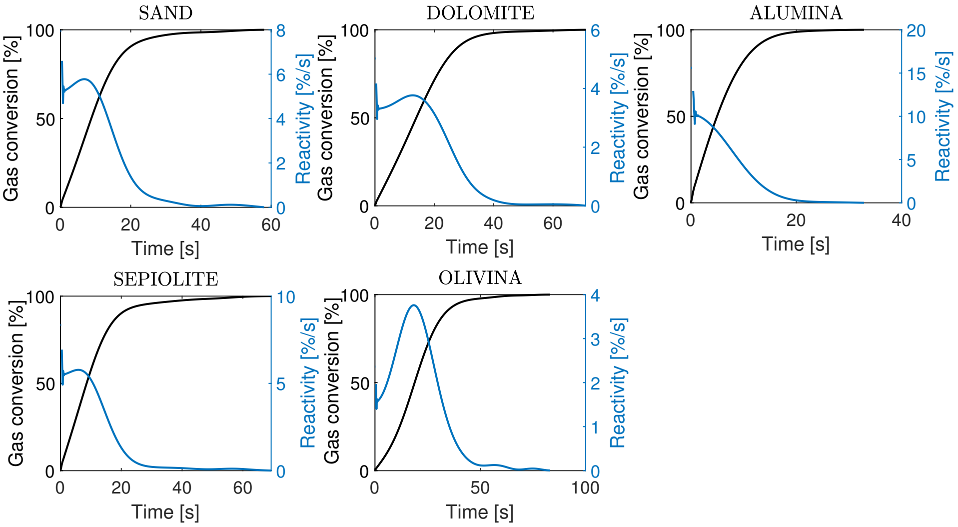


Figure 4.2: Comparison of the conversion and the reactivity among the different bed materials for wood pellets pyrolysis.

Table 4.1: Apparent kinetic constant and standard deviation of the first order model approximation, for pellets and SS pyrolysis.

	Sewage sludge				
	Sand	Dolomite	Alumina	Sepiolite	Olivina
k [1/s]	0,169	0,179	0,134	0,115	0,096
R^2	0,978	0,983	0,966	0,982	0,958
	Wood pellets				
	Sand	Dolomite	Alumina	Sepiolite	Olivina
k [1/s]	0,145	0,159	0,1198	0,1317	0,0547
R^2	0,967	0,983	0,976	0,979	0,934

The kinetic of the reaction is almost the same for the two biomass: in both cases the olivina is the material giving the slowest one, and the worst approximation, as can be seen by the standard deviation4.1. For all the rest of the materials its value ranges between 0.11 up

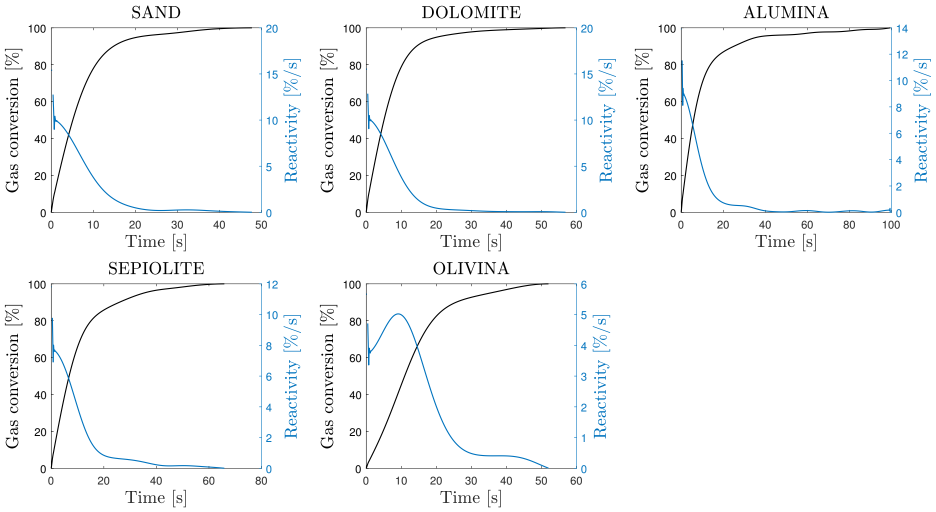


Figure 4.3: Comparison of the conversion and the reactivity among the different bed materials for sludge pyrolysis.

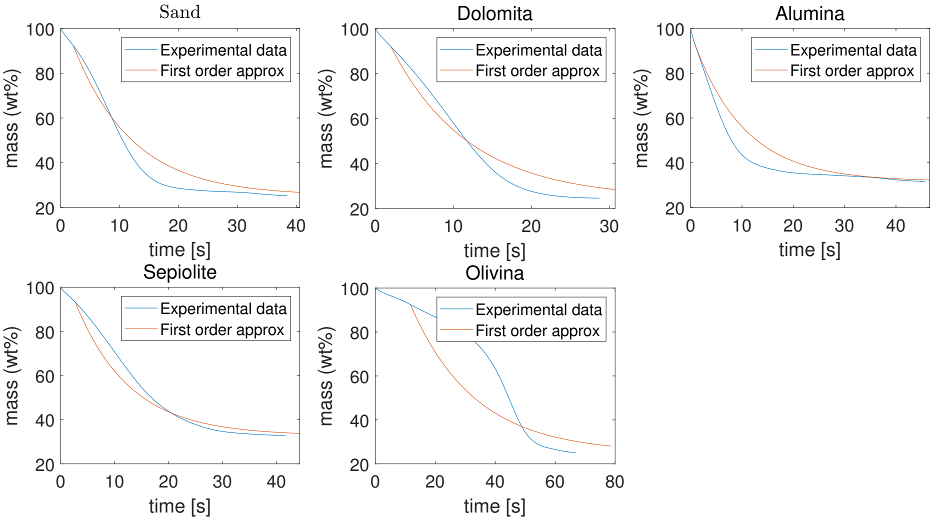


Figure 4.4: First order approximation model for wood pellets.

to 0.19 1/s: the highest value has been shown by dolomite used with the sewage sludge, demonstrating to be much more reactive toward this biomass than with wood pellets.

The pyrolysis time shown in Figure 4.6 has resulted very similar for both the biomass, and very close to the ones found in literature [72]. Staying to what previously said about the fast pyrolysis, the shorter is the t_{pyr}, the higher is the probability to obtain a higher liquid fraction: from this prospective olivine is the worst material with both the biomasses. Instead, sand seems to be the best when used with wood pellets, but we have to remember that the conversion that it offers is very modest. On the contrary, dolomita is very effective

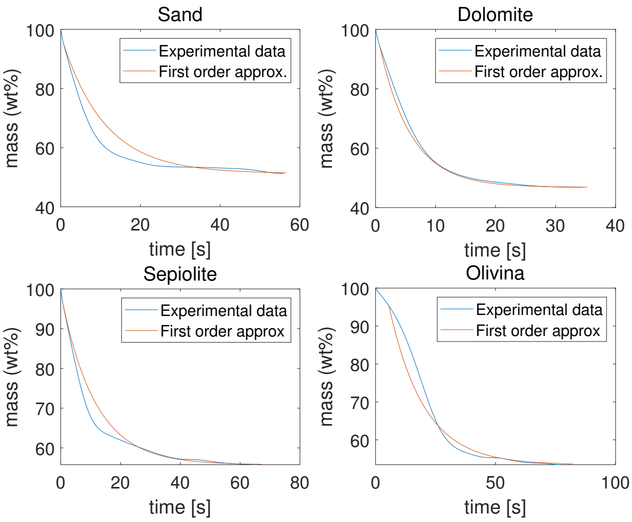


Figure 4.5: First order approximation model for sewage sludge.

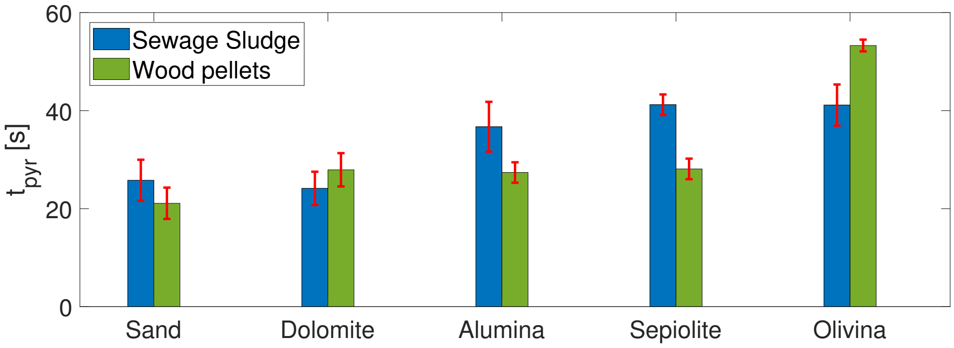


Figure 4.6: Comparison of the pyrolysis time, t_{pyr}, needed to obtain the 95 % of the conversion for both, wood pellets and sewage sludge pyrolysis

when used with SS, for both the point of view: time of reaction and conversion.

For this first experiment, the analysis of the temperature profiles and their comparison results very interesting. For the wood pellets, temperature profile and its derivative are reported in Figure 4.7.
According to the results, it appears that, all the materials dissipate the heat with the same speed when no reaction occurs, but during the reaction itself there are dierences: the reactions are endothermic for all the materials, except olivine. The endothermicity of reactions with sepiolite is a bit higher than for sand, dolomite or alumina. However, for olivine different effects are observed. At the begining of the pyrolysis, a high endothermic reactions take place. After that, the behaviour is inversed appearing exothermic reactions.
Exactly the same can be said when the sewage sludge pyrolysis is performed (Figure 4.8). But in this case, the temperature curve seems to do a step after 20 seconds from the

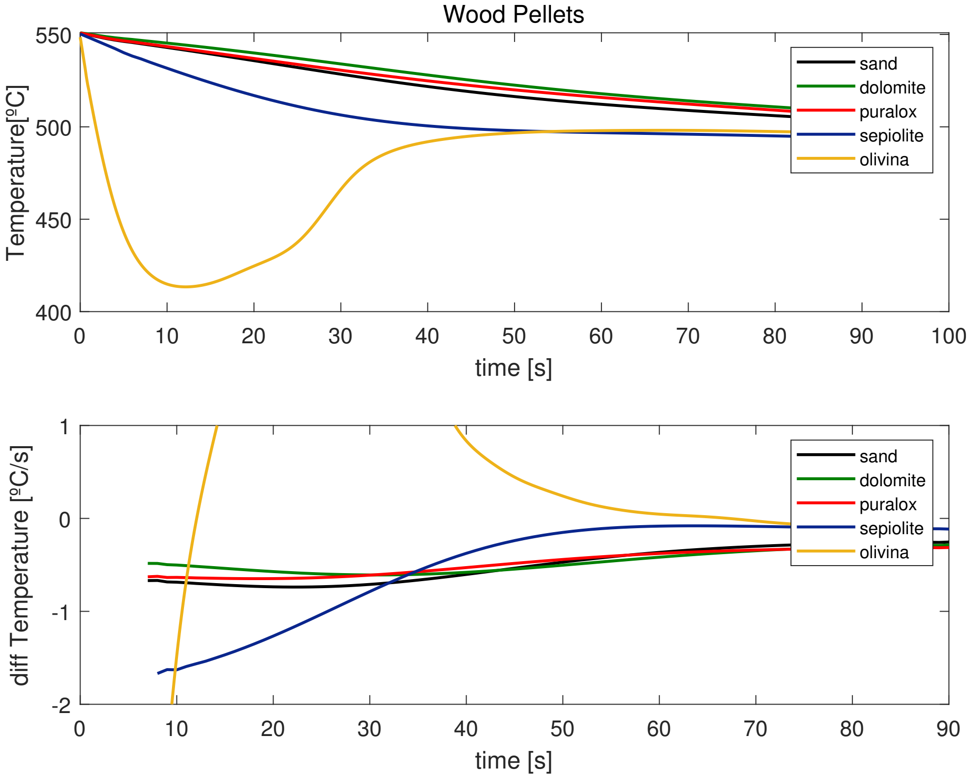


Figure 4.7: Temperature profile of the wood pellets pyrolysis, for the five bed materials.

beginning.

4.1.1 Bio-char analysis

The obtained bio-char is subjected to the BET analysis and to the measurement of its HHV value, as previously anticipated.

For what concern the BET analysis (Table 4.2), it turned out that the produced material is mesoporous in both cases and the Total Surface Area of the bio-char from the wood pellets is higher than the one from the sewage sludge. The obtained data are coherent with the ones found in literature: Weber et al.[73] reported that the Total Surface Area of the SS biochar is never over 100 m^2/g.
Differences linked with the usage of catalysts are not detected.
The porosity and the total surface area of the biochar are the results of the escaping volatile gases, and they are often considered a fundamental prerequisite for various biochar applications [73]. It is necessary to have a very high Total Surface Area to provide a proper gas adsorption for the the CO2 or the H2 storage (around 3500 m^2/g), but for other applications, such as the adsorption of contaminant reduction in soil and water, it is not a

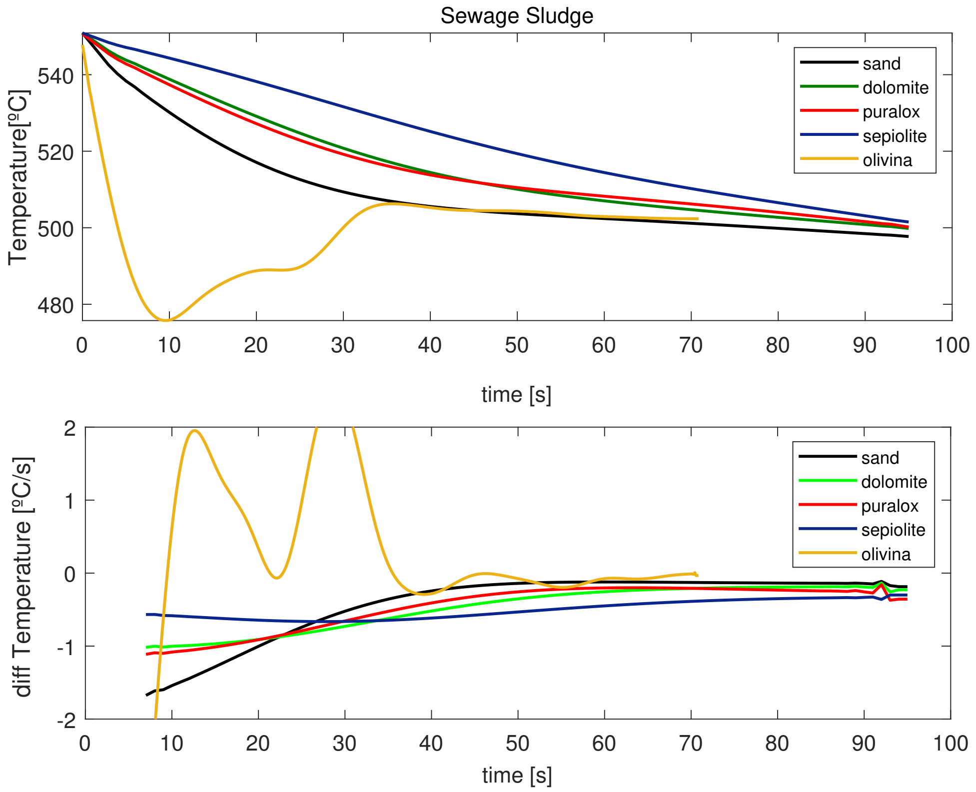


Figure 4.8: Temperature profile of the SS pyrolysis, comparing the 5 bed materials

peculiar characteristic (it can be less than 200 m^2/g), while the function groups on the biochar surface become much more important [85].
Anyway, biochar is a good raw material for making activated carbon, achievable with a thermal treatment, using temperatures ranging between 600 and 1200 in the presence of oxidizing gases, such as carbon dioxide, steam and air [85]. For what concern the results

Table 4.2: BET analysis for bio-char particles.

Bio-Char from wood pellets	
External Surface Area [m^2/g]	n.a.
Total Surface Area (BET) [m^2/g]	63,59
Bio-Char from wood sewage sludge	
External Surface Area [m^2/g]	33,95
Total Surface Area (BET) [m^2/g]	45,68

obtained via the calorimetry, the char produced from the wood pyrolysis resulted having a HHV (around 25 MJ/kg) ˜3.5 times higher that the one obtained from the sewage sludge. Among the samples obtained with different catalysts there are some variations, Figure 4.9: the alumina give the lowest HHV, while the highest is given by the olivine, reporting a gap of 1 MJ/kg. Both sand and dolomite give a value very close to the one achieved with olivine. The analysis has been repeted 3 times for each sample, reporting a standard deviation lower than 0,08 in all the cases.

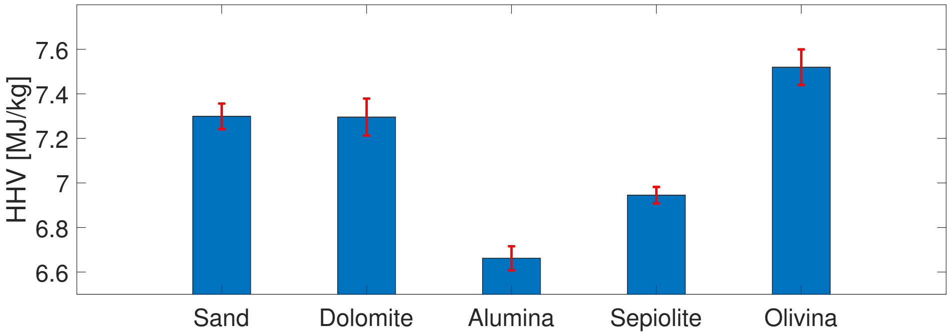


Figure 4.9: Comparison between the HHV of the different samples of char derived from sludge.

4.1.2 Biomass particle size

Pellets pyrolysis is repeated using the biomass without any previous crushing operation, in order to compare the effect that the size can have on the process. Results are summarized in Figure 4.10 and Figure 4.11. The materials reconfirmed their catalytic attitudes, but the yield is in general lower (around 15% less), and the t_{pyr} longer (almost the double) than the case with crushed pellets. The reaction rate is plotted as well, as previously done,

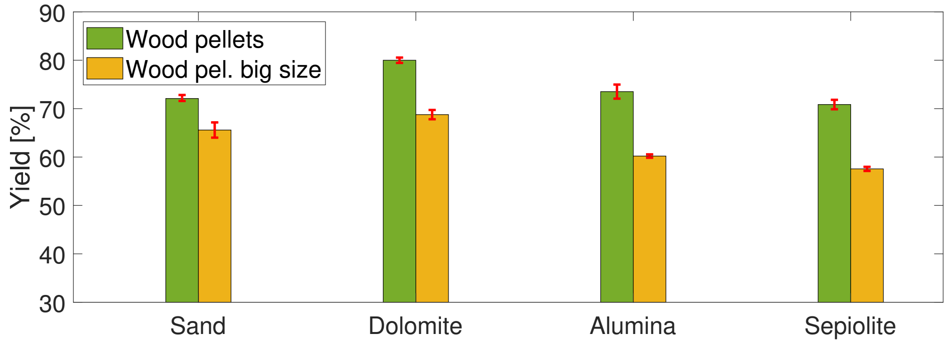


Figure 4.10: Comparison of the yields achieved with no-crushed pellets and crushed pellets pyrolysis, using different bed materials.

and, in this case, no evident variations are showed when the catalysts are used (Figure 4.12). The kinetic is also calculated, as reported in the following table, resulting much lower than the one calculated for the crushed wood pellets. As it is possible to see from Figure 4.13, and from the standard deviation reported in Table 4.3, the apparent kinetic

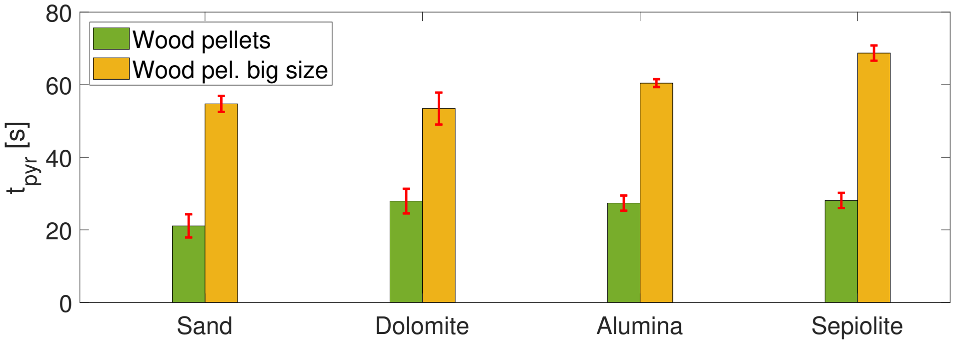


Figure 4.11: Comparison of the t_{pyr} obtained with the wood pellets with small and big particles.

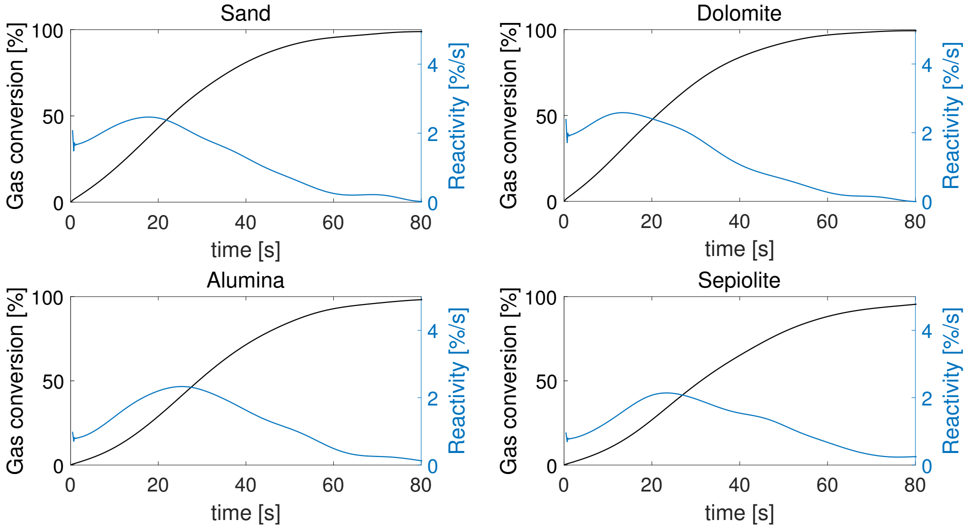


Figure 4.12: Conversion and reaction rate over time for pyrolysis of no crushed wood pellets using different bed materials.

first order model fits with the experimental data. According to these results, the size of the biomass particles has a strong influence on the pyrolysis yield and the reaction rate: the smaller is, the more is promoted the reaction, even though, there are some limitations [78]. In fact, the particle size influences the heating rate: the increase of the particle size cause the decreases of the heating transfer inside the particle and consequently the decrease of the reaction rate, of the average gasification reactivity, and the increase of yield of char. In addition, smaller particle size favours cracking of hydrocarbons with consequent increase of hydrogen yield due to longer resident time of volatiles in the reactor [8].

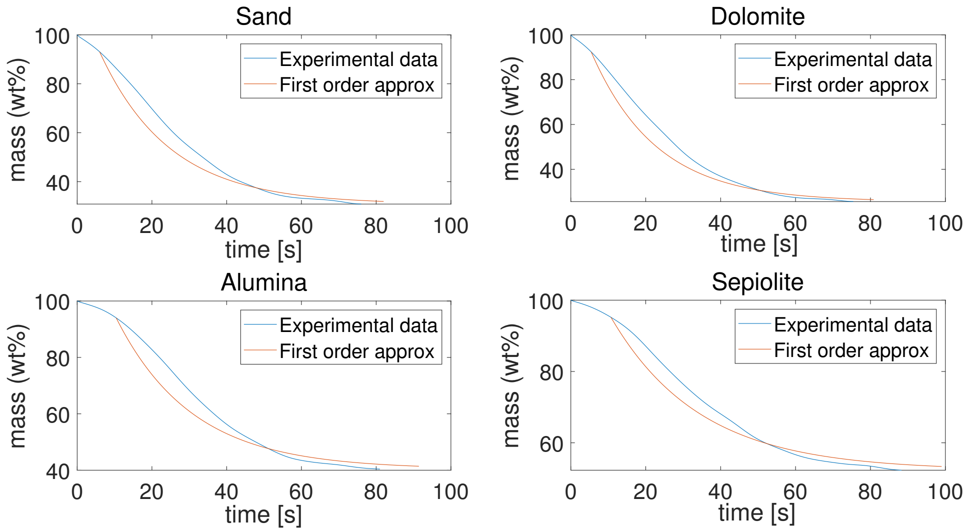


Figure 4.13: Apparent kinetic first order model compared with the experimental data.

Table 4.3: Apparent kinetic constant, yield and R^2 obtained for the big size pellets pyrolysis.

Material	sand	dolomite	alumina	sepiolite
Yield [%]	65,7	69,03	59,9	57,2
k [1/s]	0,0534	0,0575	0,042	0,0491
R^2	0,957	0,958	0,962	0,959

4.2 Deactivation phenomena

Phenomenon of deactivation is investigated. In order to discover how does it affect the performance of the reaction, two type of cycles are carried out, following the procedure described in section 3.6 and 3.7. The purpose of the first one, as previously mentioned, is to study the effects caused by the char deposition on the bed material.

Figure 4.14 shows the results for sand, dolomite and sepiolite. When sand is used as bed material, the yield increases from 74 to 80 wt.%, but with dolomite it seems to go in the opposite direction, decreasing from 82 to 76 wt.%. Instead, with sepiolite, it remains almost constant (˜69 wt.%). The aim of the second cycle is to study how the ash deposition can influence the catalytic attitudes of the bed materials. Contrarily to the previous case, the experiment was performed only with sand and dolomite. Moreover, to verify that there is a real implication of the deactivation phenomena, only for the dolomite is provided a regeneration in correspondence of the tenth repetition, with a thermal treatment at 650 °C for 2 hours. After which, other 4 repetitions are performed, to detect its impact.

Figures 4.17 show the effect of the cycles in the bed materials color: contrarily to the previous cycle performed, it occurs only after the first reaction, after which it remains constant. The yield decreases in both cases: with the sand decreases slightly passing from

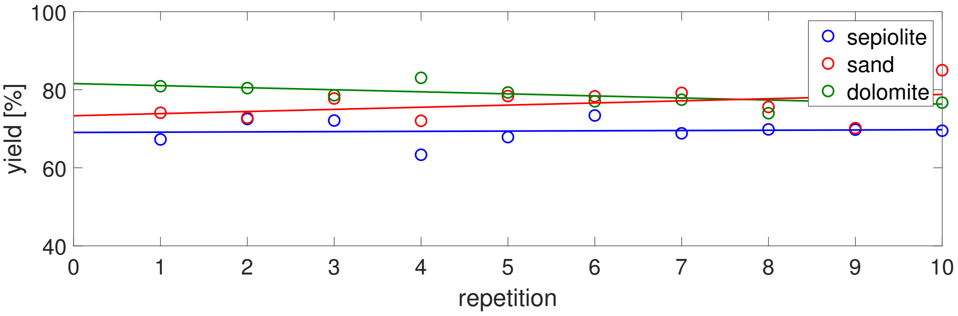
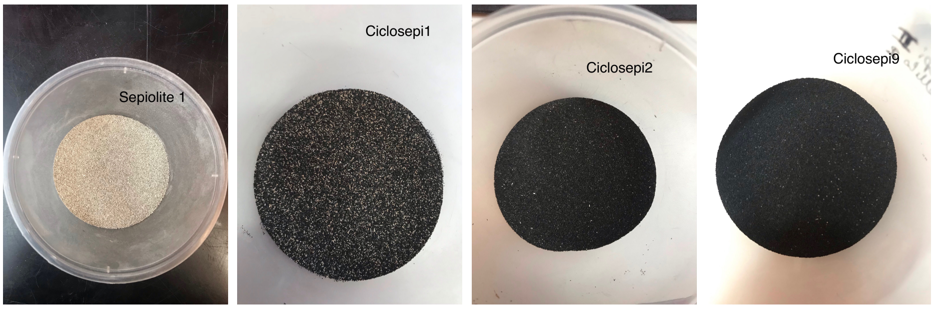


Figure 4.14: Comparison of the yields for pellets pyrolysis using sand, sepiolite and dolomite, respectively, for the first type of cycle.

(a) (b) (c) (d)

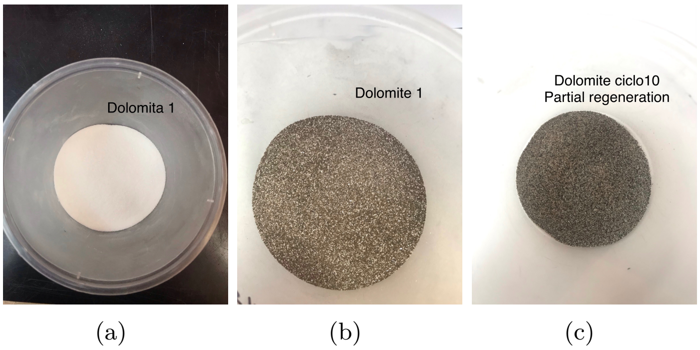
Figure 4.15: Pictures taken between one repetition and an other of the pellets pyrolysis cycle, promoting the char deposition. It can be seen that the sand get darker, passing from light yellow to black, in the last one.



(a) (b) (c) (d)

Figure 4.16: Pictures taken between one repetition and an other of the pellets pyrolysis cycle, promoting the char deposition. It can be seen that the sepiolite get darker, passing from light yellow to black, in the last one.

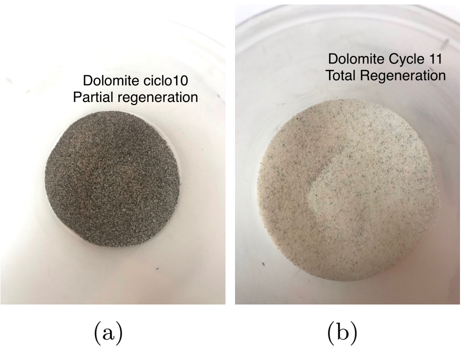
73.6 wt% to 67.7 wt%, Figure 4.19, while with dolomite the decrease is more accentuated, particularly during the first four repetitions, as reported in the Figure 4.20.



(a) (b) (c)

Figure 4.17: Pictures taken between one repetition and another of the pellets pyrolysis cycle, promoting the ash deposition. It can be seen that the dolomite get darker only after the first repetition, passing from (a) to (b), after which it remain almost of the same color until the last one (c).

The yield is not the only factor that is analyzed, indeed the kinetic as well is calculated using the Equation 2: the reaction slow down cycle after cycle, as showed in Figure 4.21. As expected, in correspondence of the tenth repetition (when complete regeneration is done), besides the change of colour observable, Figure 4.18, both the yield, Figure 4.20, and the apparent kinetic, Figure 4.21 increase, even if the values do not reach the initial ones. Subsequent values, after the regeneration, continue to decrease with the same previous slope. Similar results are obtained by Konstantinos et al. [79] who performed fast pyrolysis of wood commercial biomass. They had the possibility to distinguish the total volatile into bio-oil and gas, demonstrating that the decrease over time is attributable to the bio-oil, which is also the only fraction to be affected by the regeneration.



(a) (b)

Figure 4.18: Dolomite before (a) and after (b) of the total regeneration, tenth and eleventh cycles.

Comparing the two cycles using sand as bed material (the first with char deposition, and the second with ash deposition), it is evident that the deposited bio-char has catalytic effect on the pyrolysis. Moreover, it is deducible that sand, might have some sporadic active sites, which are covered by the formed ash, explaining the slight decrease of the yield. On the other hand, looking at the results obtained with dolomite, it is interesting

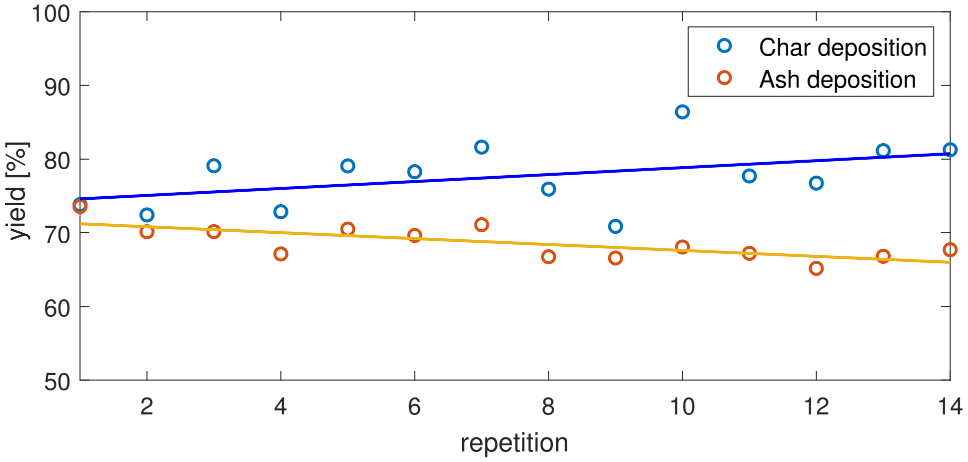


Figure 4.19: Pellets pyrolysis: yield comparison. Bed material:Sand. Char deposition vs. ash deposition.

to see how the catalytic effect of the bio-char can compensate the progressive coverage of the active sites, situated on its surface. In fact, in absence of bio-char, the yield decreases faster, up to the fourth repetition, after which it seems to follow the same trend of the ash-deposition case (the two linear regression are almost parallel).

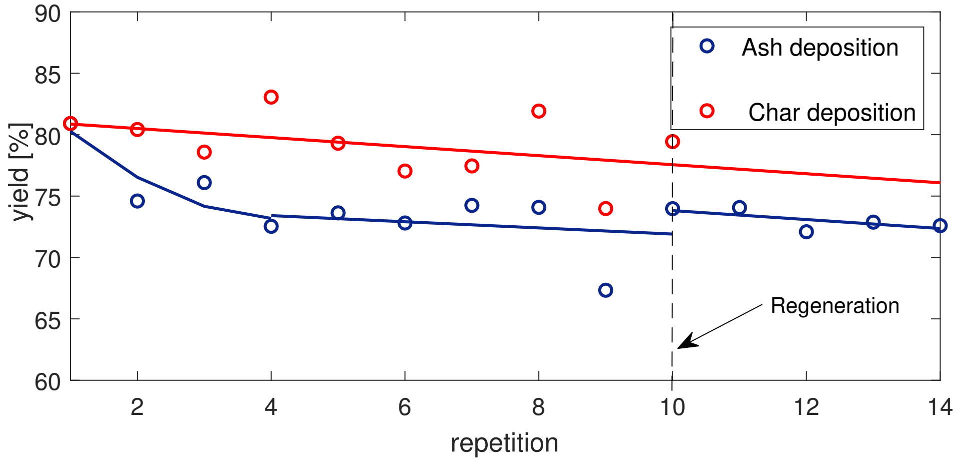


Figure 4.20: The deactivation of the dolomite is tested by comparing the yields calculated for the two cycles (one performed to test the effects of the char deposition an the other of the ash deposition). The biomass used is the wood pellets. In correspondence of the tenth repetition, a regeneration has been provided, in the only case of the ash deposition cycle

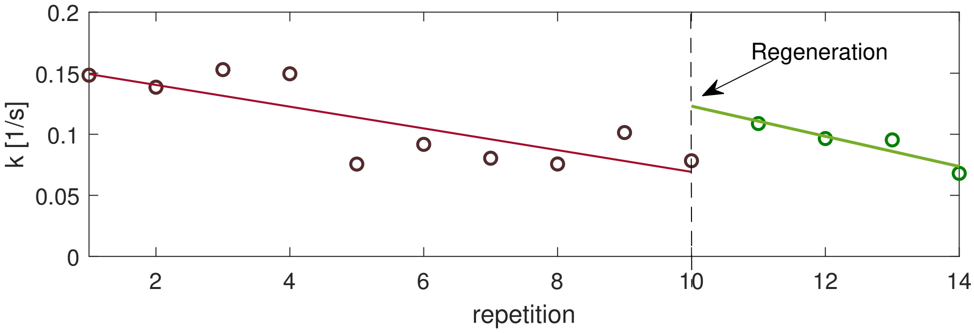


Figure 4.21: Comparison between kinetics obtained from pellets pyrolysis affected by ash deposition. After 10 repetitions a regeneration treatment has been provided. Bed material: dolomite.

4.3 Bio-char accumulation

Bio-char accumulation effect has been tested. To achieve this goal, a cycle with the following characteristics has been carried out: pellets and sludge pyrolysis have been performed five times for each biomass, and for each experiment, the sand and the bio-char accumulated during the previous reactions has been used as bed material in the successive one, as describes in section 3.8.

What is expected from the analysis of the temperature profile and its derivative, considering that there is an accumulation of char (specific heat capacity of circa 1,75 [kJ/kg K] at 550 °C) is an increase of the heat capacity of the system, and this might affect the entire reaction in several way, as reported in literature [73]. The principal consequence detected is that, going further with the number of repetition, the reaction rate decreases (Figure 4.22). In fact, as pointed out by Di Blasi et al. [80], any increase in specic heat capacity of the system (both biomass or fluidized bed) results into higher conversion time. Instead, the yield does not seem to be affected by the presence of the char, as showed by Babu and Chaurasia [81], who found that specic heat capacity does not affect the primary and secondary reaction product yields. In facts, it remains around 70 wt.% for the wood pellet and around 45 wt.% for the sewage sludge, as can be ascertained by looking at Tables 4.4 and 4.5, Figure 4.22. Further considerations are done analyzing the temperature data and its derivative $\frac{dT}{dt}$, reported in Figures 4.24 and 4.23.

Table 4.4: Yields obtained by accumulating the SS bio-char in the FBR, repetition after repetition.

Bio-char from wood pellets					
Cycle	1	2	3	4	5
Yield [%]	72,0	68,0	74,0	68,0	70,0

By the way, watching at the data obtained in both cases, pellets and sludge pyrolysis, it

Table 4.5: Yields obtained by accumulating the wood pellets bio-char in the FBR, repetition after repetition.

Bio-char from sewage sludge					
Cycle	1	2	3	4	5
Yield [%]	45,3	41,3	42,3	47,5	46,9

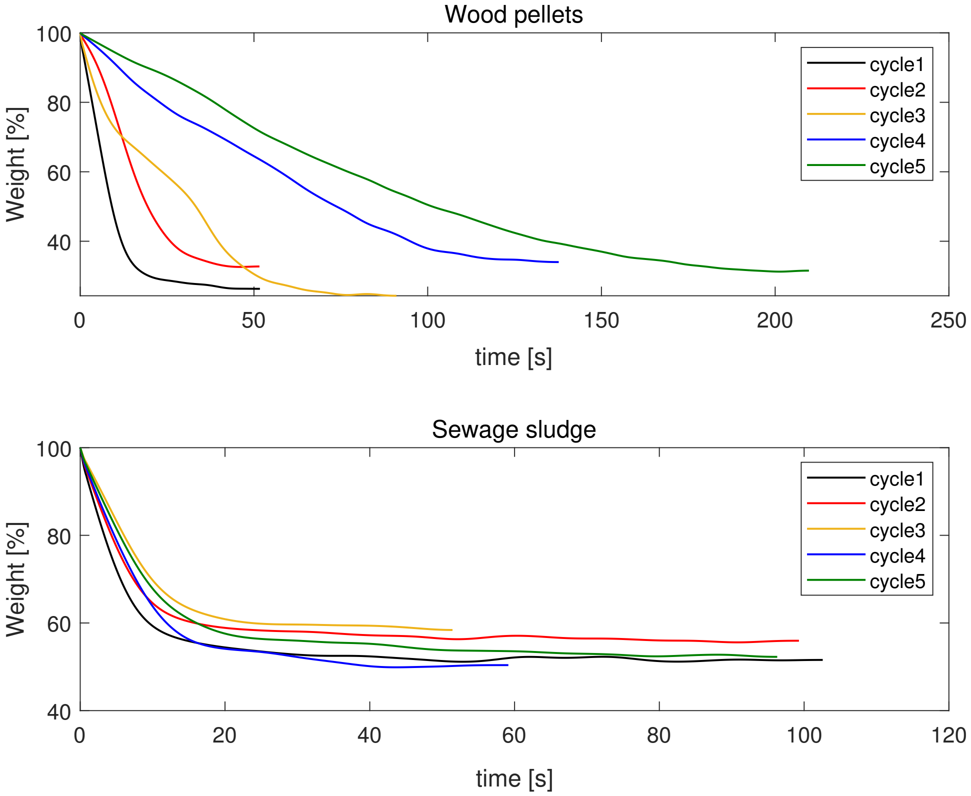


Figure 4.22: Comparison between sludge and pellets pyrolysis. Cycle with bio-char accumulation.

is possible to say that the capacity of the system to dissipate the heat does not seem to be too much affected by the presence of the bio-char in the fluidized bed, in fact the values reported as y_{max} in the tables, only increase slightly. On the contrary, the value reported as y_{min} changes more, for both the biomass, but following different trends: for wood pellets, it grows significantly, pointing out that, increasing the quantity of bio-char in the system, the endothermic absorption of reactions is less pronounced. One explanation to this phenomena might be that bio-char promotes reactions with a lower E_a (more exothermic). Differently, the y_{min} registered in the case of sludge pyrolysis drastically decreases, passing from -1.19 °C/sec in the first series to -2.69 °C/sec in the last one. It might be possible that reactions with higher E_a (more endothermic) are promoted by the bio-char. So, this might

Table 4.6: Cycle performed with the wood pellets bio-char accumulation: comparison of the $y_{cooling}$ and y_{min}

Cycle	1	2	3	4	5
$y_{cooling}$ [ºC/s]	-0,245	-0,347	-0,316	-0,307	-0,25
y_{min} [ºC/s]	-0,963	-0,528	-0,42	-0,393	-0,321

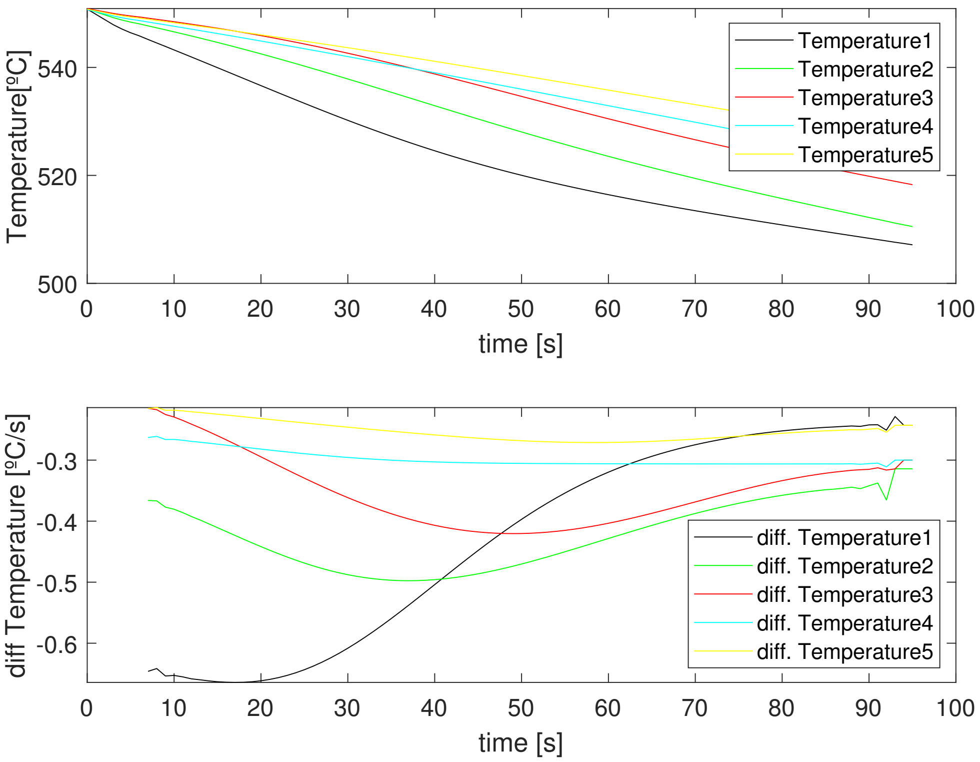


Figure 4.23: Cycle with bio-char accumulation for pellets pyrolysis.

prove that bio-oil reduction is provided, taking into account that all the reactions including volatile evaporation are endothermic, while the ones that produce char are exothermic. It is also possible to notice that in the experiment with the pellets pyrolysis, the minimum value of the temperature derivative, is shifted progressively toward right (up to 55 s in the last repetition), while in the case with sludge it is fix at the beginning of the reaction.

Instead, comparing the apparent kinetics, Eq. 3.10, it is possible to see that in both cases it decreases over time, with a similar slope, but sewage sludge displays always a higher apparent kinetic than the wood pellets (Figure 4.25).

Table 4.7: Cycle performed with the SS bio-char accumulation: comparison of the $y_{cooling}$ and y_{min}.

Cycle	1	2	3	4	5
$y_{cooling}$ [°C/s]	-0,216	-0,141	-0,0894	-0,13	-0.0682
y_{min} [°C/s]	-1,19	-2,08	-2,28	-1,64	-2,69

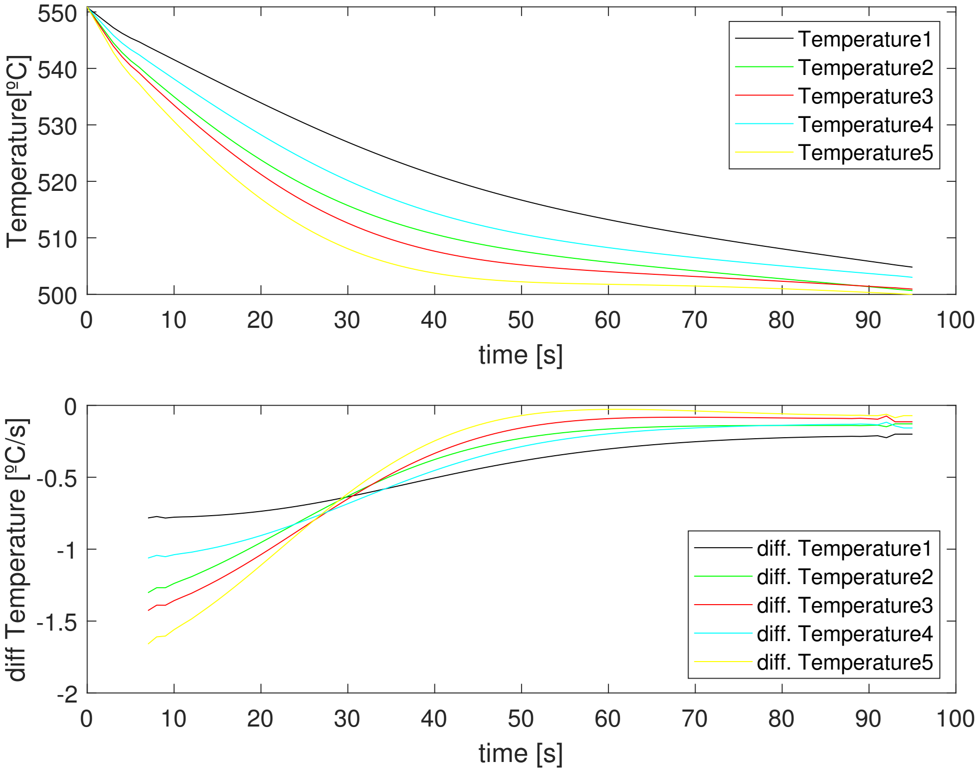


Figure 4.24: Cycle with bio-char accumulation for sludge pyrolysis

4.4 Catalytic effect of Ni-Al_2O_3

Further experiments have been provided with a Ni-Al_2O_3 catalyst, used as bed-material in the fluidized-bed reactor. In Figure 4.26, the results obtained for the two biomass (wood pellets and sewage sludge) are compared. In both cases the yield of volatile is lower for the Ni-based catalyst than the one obtained with sand. In fact, when wood pellets pyrolysis is provided, the yield obtained using Ni-based catalyst is 62.70 wt.%, 3 % lower than the one achieved with sand. The trend remains almost the same when sewage sludge is pyrolysed, but the difference between the two bed materials is smaller, less than 1 wt.% (sand 47.2 wt.% and Ni-catalyst 46.5 wt.%). Similar results were displayed by the research provided by Le et al. [82], conducted on the pyrolysis of the Alga Saccharina japonica. Also in their

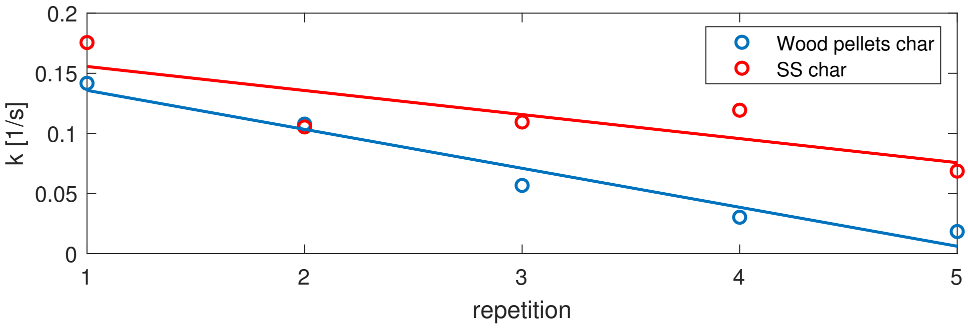


Figure 4.25: Comparison among kinetics for char accumulation experiments.

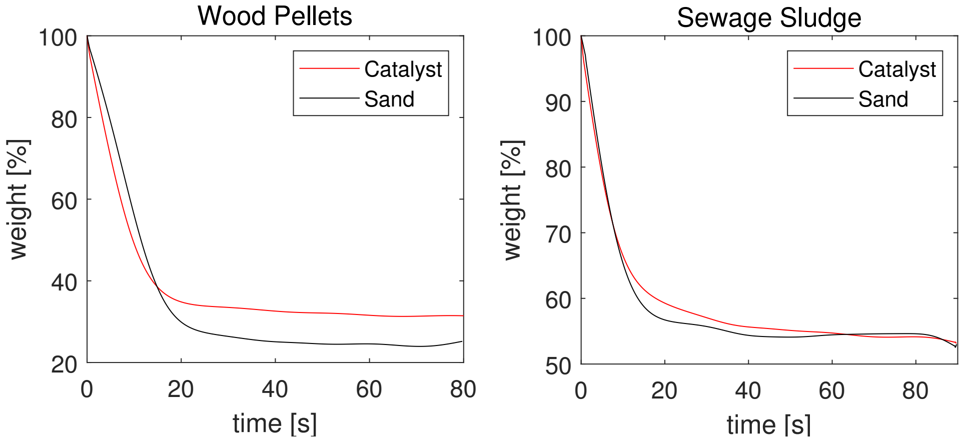


Figure 4.26: Reactivity analysis for pyrolysis of wood pellets and sewage sludge using Ni-catalyst.

experiment, the solid yield increased when the Ni-Al_2O_3 catalyst was used.

Gas conversion and reactivity curves are plotted for the pyrolysis of both, wood pellets and sludge, Figure 4.27. By the comparison of the two graphs is possible to see that the reaction with sewage sludge does not present a point of inflection, as instead happen with the wood pellets.
In the Table 4.8 are reported all the data of the apparent kinetic constant and the standard deviation: the model fits better in the case of the pyrolysis of the SS, and it has a higher k as well, as previously found for the other bed materials.
Instead, by watching to the temperature profile and its derivative in Figure 4.28, it is possible to see that the heat dispersion of the system remains almost the same when no reaction occurs, but when the reaction is running, sewage sludge carries to a faster cooling down of the system: reactions more endothermic are promoted, if compared with the wood pellets.

Table 4.8: k and R^2 obtained from the wood pellets and the SS pyrolysis, using the Ni based catalyst.

Biomass	Wood pellets	SS
k [1/s]	0,0952	0,1369
R^2	0,977	0,985

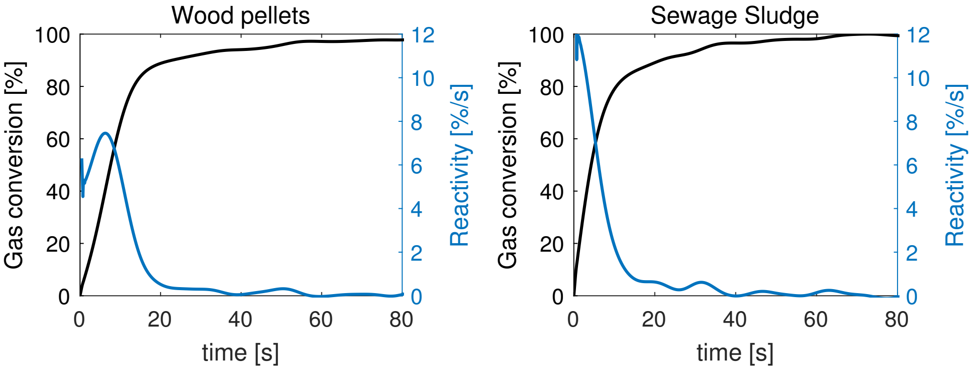


Figure 4.27: Reactivity analysis for pyrolysis of wood pellets and sewage sludge using Ni-catalyst.

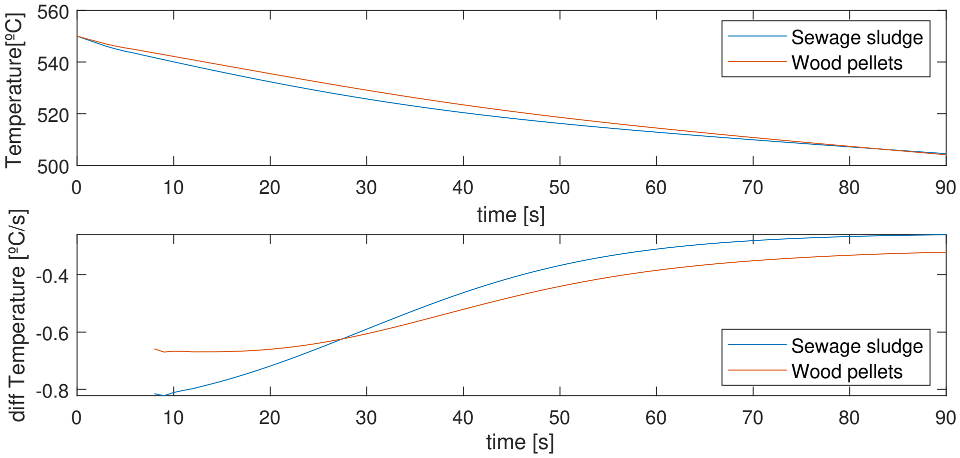


Figure 4.28: Temperature analysis for pyrolysis of wood pellets and sewage sludge using Ni-catalyst.

Chapter 5

Conclusion and future works

The pyrolysis process was significantly influenced by the use of the catalysts as fluidized bed: especially the dolomite was the material that, in general, has provided the best performances, improving the yield of volatiles of ~10 wt%, for both the biomass types. In particular it achieved good results with the sewage sludge, obtaining the highest apparent kinetic and the shortest time of pyrolysis.

Thought, dolomite demonstrated to be highly sensitive toward the deactivation phenomenon, performing a decrease of the yield of 6 wt.% and of the apparent kinetic (suffering a deceleration of the 42 % from the first value displayed), after 10 cycles. However, as experimentally demonstrated, it can be partially recovered by providing a regeneration. It would be interesting to repeat the experiment including also calcined dolomite, and verify if it is more reactive and efficient than the natural one.

Olivine has also showed a good capacity to improve the yield, but performing always the slowest apparent kinetic, reporting a different trend of the reaction rate curve and temperature profile.

Instead, the Ni-γAl_2O_3 did not displayed the expected results, providing a lower volatile yield than the one reached with sand.

The first-order apparent kinetics model appears valid in the description of small particles of sewage sludge in the bubbling fluidized bed, where heat and mass transfer effects are negligible. Only in the case with the olivine, discrepancies were found between the model predictions and the experimental measurements.

For what concern the particle size, it had a strong impact on the reaction: when larger particles have been tested, the yield of volatile decreased of 15 wt.% and the kinetic of the reaction became 3 times slower, doubling the time of pyrolysis. In general the effects produced by the catalysts presence were less pronounced.

Also the deposited char has demonstrated good catalytic proprieties, achieving high volatile yield, reaching almost the same ones performed by the dolomite. Staying at the most recent research on the field, secondary reactions, such as vapour phase cracking, occur on the bio-char surface.

The use of the bio-char as a catalyst for a up-grading in situ application, could be considered an available route to improve the pyrolysis process, taking into account that it is not affected by deactivation problem, it is automatically recovered during the process itself, and it has no additional costs. Of course, future studies should investigate on its capacity to upgrade the bio-oil quality, because the only increase of volatile yield it is not enough to consider it a good option.

Concerning possible utilization of the produced bio char, its surface area do not results high enough to remove contaminants from gas, so it is necessary to perform a previous activation (chemical or physical) to obtain activated carbon with a high surface area. So, future studies focused on this field could be interesting.

5.1 Future improvements

As before underlined, this work is only a small part of the entire optimization process. In fact, once that the bed material has been individuated as the most promising, it is necessary to test it in a pilot plant, including a refrigeration system to condense and extract the liquid from the entire amount of volatile released during the pyrolysis. This liquid product might be subjected to further separation from the water by decantation.

This step is fundamental, making possible the calculation of the liquid and bio-oil yield, and the analysis of its properties, such as HHV, viscosity, composition with CHN, FTIR, TGA (to detect oxygenates and aromatics compounds in particular), aging phenomena, etc.

Moreover, for the identication of the volatile compounds, a gas chromatograph coupled to a mass spectrometry detector (GC-MS) might be useful and it can become a tool even more powerful, if it is coupled wit a flame ionization detector (Py-GC-MS/FID), giving the possibility to do, at the same time, qualitative and quantitative investigation on the product distribution.

To explore deeper the nature of the deactivation phenomenon that affects the cataysts, might be interesting to study the evolution of their surface chemistry during their use as bed material in a FBR, performing analysis as BET, SEM-EDX, XRD, XPS, and TPO/TPD.

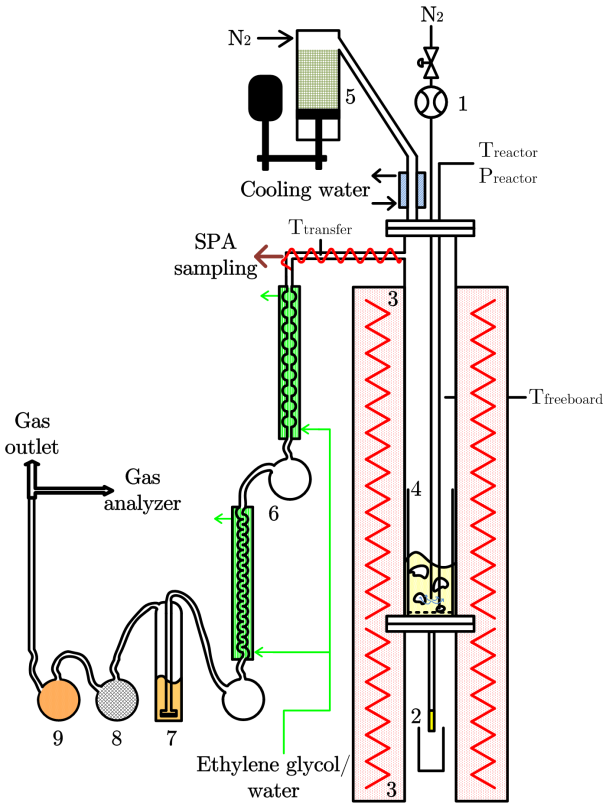


Figure 5.1: Schematic rappresentation of a pilot plant for the biomass pyrolysis and liquid extraction.

Acronyms

MRC Maximal Ratio Combining

BET Brunauer Emmett Teller

CFB Circulating Fluidized Bed

daf dry ash free

FBR Fluidized Bed Reactor

GC Gas Cromatography

HHV High Heating Value

IPPC Integrated Pollution Prevention and Control

IUPAC International Union of Pure and Applied Chemistry

LHV Low Heating Value

MS Mass Spectrometry

PCS Potere Calorifico Superiore

SEM Scanning Electron Microscope

SS Sewage Sludge

TGA Thermogravimetric Analysis

TPD Temperature Programmed Desorption

TPO Temperature Programmed Oxidation

XRD X-ray Powder Diffraction

List of Symbols

d_{bm}	Diameter of the bed material particles
d_i	Inner diameter of the reactor
E_a	Activation energy
ϵ	Void fraction of the dense phase particles
g	Gravitational acceleration
h	Reactor height
h_b	Fixed-bed height
k	Apparent kinetic constant
$\dot{m}$	Gas mass flow
$m_{char+ash}$	Sum of the char and ash mass
m_{fin}	Final mass registered by the precision scale
m_o	Initial mass of biomass
m_{vol}	Mass of volatile
$m_{vol,0}$	Initial mass of volatile
n	Order of the reaction
r_{vol}	Reactivity of the biomass
R^2	Correlation coefficient
S_{react}	Section of the reactor
t_{fin}	Final time: stabilization of the signal
T	Temperature
T_{pyr}	Operative temperature of the pyrolysis
t_{pyr}	Time to reach the 95% of the conversion
U	Velocity of the fluidizing agent
U_{mf}	Minimum fluidization velocity
$\dot{V}$	Gas volume flow
χ	Conversion
$y_{cooling}$	Minimum point of the absolute value of the temperature derivative
y_{max}	Maximum point of the temperature derivative
y_{min}	Minimum point of the temperature derivative
ν_g	Gas viscosity
ρ_{bm}	Density of the bed material
ρ_g	Gas density
ϕ	Sphericity

Il listato del pacchetto `topcoman.sty`

```
%%
%% This is file ‘topcoman.sty’,
%% generated with the docstrip utility.
%%
%% The original source files were:
%%
%% toptesi.dtx  (with options: ‘topcmn’)
%%   ------------------------------------------------------
%%   The TOPtesi bundle
%%   Copyright (C) 2015-2018 Claudio Beccari
%%   All rights reserved
%%
%%   License information appended
%%
\NeedsTeXFormat{LaTeX2e}[2016/01/01]
\ProvidesPackage{topcoman}[%
2018/05/06 v.~6.2.04
Additional commands for the TOPtesi bundle]


\RequirePackage{iftex}
\ifPDFTeX
\newcommand*\DeclareSlantedCapitalGreekLetters{%
   \mathchardef\Gamma="7100
   \mathchardef\Delta="7101
   \mathchardef\Theta="7102
   \mathchardef\Lambda="7103
   \mathchardef\Xi="7104
   \mathchardef\Pi="7105
   \mathchardef\Sigma="7106
   \mathchardef\Upsilon="7107
   \mathchardef\Phi="7108
   \mathchardef\Psi="7109
   \mathchardef\Omega="710A
}\else
\newcommand*\DeclareSlantedCapitalGreekLetters{%
```

```
\PackageWarning{toptesi}{%
   When using LuaLaTeX or XeLaTeX specify\MessageBreak
   option math-style=ISO to package unicode-math\MessageBreak}
}
\fi
\providecommand*\ensuremath[1]{\ifmmode#1\else$#1$\fi}%
\providecommand*\textormath{}
\renewcommand*\textormath{\ifmmode\expandafter\@secondoftwo\else
    \expandafter\@firstoftwo\fi}
\providecommand*\textsubscript{\raisebox{-0.5ex}}

\ifPDFTeX
\@ifpackageloaded{textcomp}{}{\RequirePackage{textcomp}}
\fi
\providecommand{\ohm}{\textormath{\textohm}{\mathrm{\Omega}}}
\@ifpackageloaded{toptesi}{%
\providecommand\ped{}\providecommand\ap{}
\renewcommand*{\ped}[1]{\textormath{\textsubscript{#1}}{_{\mathrm{#1}}}}
\renewcommand*{\ap}[1]{\textormath{\textsuperscript{#1}}{^{\mathrm{#1}}}}}{%
\providecommand*{\ped}[1]{\textormath{\textsubscript{#1}}{_{\mathrm{#1}}}}%
\providecommand*{\ap}[1]{\textormath{\textsuperscript{#1}}{^{\mathrm{#1}}}}}
\@ifpackageloaded{siunitx}{\def\unit#1{\si{\,#1}}}{%
\providecommand\unit{}%
\renewcommand\unit[1]{\ensuremath{{\mathrm{\,#1}}}}
}
\providecommand{\gei}{\ensuremath{{\mathop{\mathrm{j}}\nolimits}}}
\providecommand{\eu}{\ensuremath{{\mathop{\mathrm{e}}\nolimits}}}
\providecommand{\micro}{\textormath{\textmu}{%
  \ifPDFTeX
    \ifdefined\muup\muup\else\mbox{\textmu}\fi
  \else
    \mathup{\mu}%
  \fi
}}
\providecommand{\gradi}{\textormath{\textdegree}{^\circ}}
\RequirePackage{fancyvrb}
\fvset{fontsize=\small}
\let\listing\VerbatimInput
\DeclareRobustCommand*{\fakeSC}[1]{%
{\dimen@=\f@size\p@\dimen@=0.75\dimen@
\fontsize{\dimen@}{\f@baselineskip}\selectfont
\expandafter{\uppercase{#1}}}}%
\ifPDFTeX\let\simulatedSC\fakeSC\else\let\simulatedSC\textsc\fi
\def\ft@figure{\iflanguage{italian}{\MakeLowercase{\figurename}}%
            {\figurename}~}
\def\ft@table{\iflanguage{italian}{\MakeLowercase{\tablename}}%
            {\tablename}~}
\newcommand*\EnableFigTabNames{%
            \let\p@figure\ft@figure\let\p@table\ft@table}
\newcommand*\DisableFigTabNames{%
```

```
            \let\p@figure\empty\let\p@table\empty}
\DisableFigTabNames
%%
%% Copyright 2005-2018 Claudio Beccari
%%
%% Distributable under the LaTeX Project Public License,
%% version 1.3c or higher (your choice). The latest version of
%% this license is at: http://www.latex-project.org/lppl.txt
%%
%% This work is "author-maintained"
%%
%% This work consists of this file toptesi.dtx, a README file
%% the manifest.txt file, and the derived files:
%%     toptesi.cls,
%%     toptesi.sty,
%%     topfront.sty,
%%     topcommand.sty,
%%     toptesi-scudo.sty,
%%     toptesi.cfg,
%%     toptesi-monografia.sty,
%%     toptesi-sss.sty,
%%     toptesi-magistrale.sty,
%%     toptesi-dottorale.sty,
%% and the English documentation toptesi.pdf.
%%
%% Furthermore the bundle contains the documentation source
%% file toptesi-it.tex and the derived file
%% toptesi-it.pdf.
%%
%% The toptesi-example.tex source file is just an example
%% that shows how to use the various commands; by commenting
%% or uncommenting certain source lines it is possible to
%% typeset different kind of theses and their front pages.
%%
%% The topfront-example.tex source file is an example of how
%% to produce just the title page with TOPtesi and the external
%% package frontespizio.
%%
%% The toptesi-scudo-example.tex source file is an example
%% that shows the particular features available with TOPtesi,
%% when a doctoral thesis is produced for the Scuola di
%% Dottorato (ScuDo) of Politecnico di Torino.
%%
%% The toptesi.cfg file is a sample of a local configuration
%% file that can be copied to another file and its copy freely
%% edited and customised.
%%
%% The other toptesi-*.sty files are extension modules for
%% typesetting the specific thesis kinds described by the
%% suffix that replaces the asterisk.
```

```
%%
%% By running pdflatex on toptesi.dtx the user gets the class,
%% sty and cfg files and the English documentation file in
%% PDF format.
%%
%% The source file of the Italian documentation file
%% toptesi-it.pdf is another example of how to use TOPtesi.
%% This file toptesi-it.tex may be typeset with pdfLaTeX,
%% XeLaTeX, and LuaLateX; see the first comment lines of
%% the file for how-to information. In spite of being mainly
%% written in Italian, it contains several sections in English
%% for the benefit of foreign students attending the Doctoral
%% School of Turin.
%%
%% End of file ‘topcoman.sty’.
```

Bibliography

[1] Pant K.K. and Mohanty, *Transformation of Biomass: Theory to Practice*, First Edition. Edited by Andreas Hornung. 2014 John Wiley & Sons, Ltd. Published 2014 by John Wiley & Sons, Ltd. Companion website: http://booksupport.wiley.com.

[2] Dhyani V., Bhaskar T., *A comprehensive review on the pyrolysis of lignocellulosic biomass*, India Renewable Energy 129 (2018) 695-716.

[3] Fontsa I., Geab G., Azuarab M., Ãbregoc J., Arauzob J., *Sewage sludge pyrolysis for liquid production: A review*, Renewable and Sustainable Energy Reviews 16 (2012) 2781-2805

[4] Basu P., *Biomass gasification and pyrolysis : practical design and theory*, 2010 Published by Elsevier ISBN 978-0-12-374988-8.

[5] https://ec.europa.eu/energy/en/topics/energy-strategy-and-energy-union/2050-long-term-strategy, last access: september 2019.

[6] Martinsa F., Felgueirasb V., Smitková M., *Fossil fuel energy consumption in European countries*, 5th International Conference on Energy and Environment Research, ICEER 2018 (https://creativecommons.org/licenses/by-nc-nd/4.0/).

[7] Ecofys – A Navigant Company, and Stockholm Environment Institute, *Technical assistance in realisation of the 2018 report on biofuels sustainability Biofuels, biomass & biogas used for renewable energy generation*, 2019, Project number: SISNL17791 / 147631.

[8] Hu X., Gholizadeh M., *Biomass pyrolysis: A review of the process development and challenges from initial researches up to the commercialisation stage*, Journal of Energy Chemistry, 39 (2019) 109–143

[9] Sharma A., Pareek V., Zhang D., *Biomass pyrolysis—A review of modelling, process parameters and catalytic studies*, Renewable and Sustainable Energy Reviews, 50 (2015) 1081–1096.

[10] Chew T.L., Bhatia S., *Catalytic processes towards the production of biofuels in a palm oil and oil palm biomass-based biorefinery*, Bioresource Technology, 99 (2008) 7911-7922.

[11] Campuzano F., Brown C.R., Martínez J.D., *Auger reactors for pyrolysis of biomass and wastes*, Renewable and Sustainable Energy Reviews, 102 (2019) 372-409 .

[12] Garcìa-Pérez M., Chaala A., Pakdel H., Kretschmer D., Rodrigue D., Roy C., *Multiphase Structure of Bio-oils*, Energy Fuels, 20 (2006) 364-375.

[13] Roslam W.N., Mohamed W.I., Hishama W.M., Yarmo M.A., Hin T.Y., *A review on bio-oil production from biomass by using pyrolysis method Author links open overlay panel*, Renewable and Sustainable Energy Reviews, 16 (2012) 5910-5923.

[14] Chew T.L., Bhatia S.,*Catalytic processes towards the production of biofuels in a palm oil and oil palm biomass-based biorefinery*, Bioresource Technology, 99 (2008) 7911–7922.

[15] Sharifzadeh M., Sadeqzadeh M., Guo M., Borhani T.N., Konda N.V.S.N.M., Cortada-Garcia M., Wang L.,Hallett J.,Shah N.,*The multi-scale challenges of biomass fast pyrolysis and bio-oil upgrading: Review of the state of art and future research directions*, Progress in Energy and Combustion Science, 71 (2019) 1–80.

[16] MoratoGodino A., Sánchez-Delgado S., García-Hernando N., Soria-Verdugo A., *Pyrolysis of Cynara cardunculus L. samples - Effect of operating conditions and bed stage on the evolution of the conversion*, Chemical Engineering Journal, 351 (2018) 371-381.

[17] Escrivani-Guedesa R., Lunaa A. S., Rodrigues-Torres A., *Operating parameters for bio-oil production in biomass pyrolysis: A review*, Journal of Analytical and Applied Pyrolysis, 129 (2018) 134-149

[18] Omar R., Idris A., Yunus R., Khalid K., Isma M.I.A., *Characterization of empty fruit bunch for microwave-assisted pyrolysis*, Fuel, 90 (2011) 1536-1544.

[19] Akhtar J., Saidina Amin N., *A review on operating parameters for optimum liquid oil yield in biomass pyrolysis*, Renew. Sustain. Energy Rev., 16 (2012) 5101-5109.

[20] Qu T., Guo W., Shen L., Xiao J., Zhao K., *Experimental study of biomass pyrolysis based on three major components: hemicellulose, cellulose, and lignin*, Ind. Eng. Chem. Res., 50 (2011) 10424-10433.

[21] Lim C.H., Mohammed I.Y., Abakr Y.A., Kazi F.K., Yusup S., Lam H.L., *Novel inputoutput prediction approach for biomass pyrolysis*, J. Clean. Prod., 136 (2016) 51-61.

[22] Pattiy A. , Suttibak S., *Production of bio-oil via fast pyrolysis of agricultural residues from cassava plantations in a fluidised-bed reactor with a hot vapour filtration unit*, J. Anal. Appl. Pyrolysis, 95 (2012) 227-235.

[23] Fu P., Hu S., Xiang J., Li P., Huang D., Jiang L., Zhang A., Zhang J., *FTIR study of pyrolysis products evolving from typical agricultural residues*, J. Anal. Appl. Pyrolysis, 88 (2010) 117-123.

[24] Hu X., Guo H., Gholizadeh M., Sattari B., Liu Q., *Pyrolysis of different wood species: Impacts of C/H ratio in feedstock on distribution of pyrolysis products*, Biomass and Bioenergy, 120 (2019) 28-39.

[25] Soja G., Frišták V., Pipíška M., *Pyrolysis treatment of sewage sludge: a promising way to produce phosphorus fertilizer*, J. Clean. Prod., 172 (2018) 1772-1778.

[26] Dai Q., Ren N., Ma L., Ning P., Qu G., Guo Z., Xie L., *Research on dewaterability and properties of sewage sludge under modified phosphogypsum and acetic acid pretreatments*, Bioresour. Technol., 264 (2018) 268-276.

[27] Ledakowicza S., Stolareka P., Malinowskib A., Lepezc O., *Thermochemical treatment of sewage sludge by integration of drying and pyrolysis/autogasification*, Renewable and Sustainable Energy Reviews, 104 (2019) 319-327.

[28] Samolada M. C., Zabaniotou A. A., *Comparative assessment of municipal sewage sludge incineration, gasification and pyrolysis for a sustainable sludge-to-energy management in Greece.*, Waste Manag, 34 (2014) 411-20.

[29] Richards G.N., Zheng G.C., *Influence of metal-ions and of salts on products from pyrolysis of wood applications to thermochemical processing of newsprint and biomass.*, J Anal Appl Pyrolysis, 21 (1991) 133-46.

[30] Fonts I., Azuara M., Gea G., Murillo M.B., *Study of the pyrolysis liquids obtained from different sewage sludge.*, J. Anal. Appl. Pyrolysis, 85 (2009) 184-91.

[31] Bridle T.R., Campbell H.W., Sachdev A., Marvan I., *Presented at the proceedings Canadian chemical engineering conference.*, 1983.

[32] Campbell H.W., Bridle T.R., *Conversion of sludge to oil - a novel-approach to sludge management*, Water Sci. Technol., 18 (1988) 1467-1475.

[33] Park H.J., Heo H.S., Park Y.K., Yim J.H., Jeon J.K., Park J., *Clean bio-oil production from fast pyrolysis of sewage sludge: effects of reaction conditions and metal oxide catalysts*, Bioresour Technol., 101 (2010) S83-5.

[34] Gerasimov G., Khaskhachikh V., Potapov O., Dvoskin G., Kornileva V., Dudkina L., *Pyrolysis of sewage sludge by solid heat carrier*, Waste Management, 87 (2019) 218-227.

[35] Richardson Y., Blin J., Julbe A., *A short overview on purification and conditioning of syngas produced by biomass gasification: catalytic strategies, process intensification and new concepts*, Prog. Energy Combust. Sci., 38 (2012) 765-781.

[36] Koppatz S., Pfeifer C., Hofbauer H.,*Comparison of the performance behaviour of silica sand and olivine in a dual fluidised bed reactor system for steam gasification of biomass at pilot plant scale*, Chemical Engineering Journal, 175 (2011) 468-483.

[37] Lin W., Dam-Johansen K., Frandsen F., *Agglomeration in bio-fuel fired fluidized bed combustors.*, Chemical Engineering Journal, 96 (2003) 171-185.

[38] Burton A., Wu H., *Quantification of Interactions between Sand and Pyrolyzing Biomass Particles in Fluidized-Bed under Fast Pyrolysis Conditions Pertinent to Bio-Oil Production*, Ind. Eng. Chem. Res., 54 (2015) 7990-7997.

[39] Skrifvars B., Hupa M., Backman R., Hiltunen M., *Sintering mechanisms of FBC ashes*, Fuel, 73 (1994) 171-176.

[40] Balci S., *Effect of heating and acid pore size distribution pre-treatment of sepiolite*, Clay Minerals, 34 (1999) 647-655.

[41] Inagaki S., Fukushima Y., Doi H., Kamigaito O., *Pore size distribution and adsorption selectivity of sepiolite*, Clay Minerals, 25 (1990) 99-105.

[42] Veses A., Aznar M., López J.M., Callén M.S., Murillo R., García T., *Production of upgraded bio-oils by biomass catalytic pyrolysis in an auger reactor using low cost materials*, Fuel, 141 (2015) 17-22.

[43] Ly H.V., Lim D.H., Sim J.W., Kim S.S., Kim J., *Catalytic pyrolysis of tulip tree (Liriodendron) in bubbling fluidized-bed reactor for upgrading bio-oil using dolomite catalyst*, Energy, 162 (2018) 564-575.

[44] Valle B., Aramburu B., Santiviago C., Bilbao J., Gayubo A.G., *Upgrading of Bio-Oil in a Continuous Process with Dolomite Catalyst*, Energy Fuels, 28 (2014) 6419-6428.

[45] Conesa J.A., Domene A., *Gasification and Pyrolysis of Posidonia oceanica in the Presence of Dolomite*, Journal of Analytical and Applied Pyrolysis, 113 (2015) 680-689.

[46] Tursunov O., *A comparison of catalysts zeolite and calcined dolomite for gasproduction from pyrolysis of municipal solid waste (MSW)*, Ecological Engineering, 69 (2014) 237-243.

[47] Sutton D., Kelleher B., Ross J.R.H., *Review of literature on catalysts for biomass gasification*, Fuel Process. Technol., 73 (2001) 155-173.

[48] Sasol, *HIGH-PURITY ALUMINA HYDRATES*, $https : //www.sasolgermany.de/index.php?id = high_purity_aluminas0$, last visit: September 2019.

[49] Matsuoka K., Shimbori T., Kuramoto K., Hatano H., Suzuki Y., *Reforming of Woody Biomass in a Fluidized Bed of Iron Oxide-Impregnated Porous Alumina* Energy Fuels 20(2006)-2727.

[50] Yorgun S., Sbimsbek Y.E., *Catalytic pyrolysis of Miscanthus B giganteus over activated alumina*, Bioresource Technology 99 (2008) 8095-8100.

[51] Shao J., Yan R., Chen H., Yang H.,Lee D.H.,*Catalytic effect of metal oxides on pyrolysis of sewage sludge*, Fuel Process.Technol., 91 (2010) 1113-1118.

[52] Aysua T., Durak H., *Catalytic pyrolysis of liquorice (Glycyrrhiza glabra L.) in a fixed-bed reactor: Effects of pyrolysis parameters on product yields and character*, Journal of Analytical and Applied Pyrolysis, 111 (2015) 156-172.

[53] Shadangi K.P., Mohanty K., *Thermal and catalytic pyrolysis of Karanja seed to produce liquid fuel*, Fuel, 115 (2015) 434-42.

[54] Azuara M., Fonts I., Barcelona P., Murillo M.B., Gea G,emphStudy of catalytic post treatment of the vapours from sewage sludge pyrolysis by means of γ Al2O3, Fuel, 107 (2013) 113-21.

[55] Stefanidis S.D., Kalogiannis K.G., Iliopoulou E.F., Lappas A.A., Pilavachi, *In-situ upgrading of biomass pyrolysis vapors: catalyst screening on a fixed bed reactor.*, Bioresour Technol., 102 (2011) 8261-7.

[56] Kaewpengkrow P., Atong ., Sricharoenchaikul V,emphEffect of Pd, Ru, Ni and ceramic supports on selective deoxygenation and hydrogenation of fast pyrolysis Jatropha residue vapors., Renew. Energy, 65 (2014) 92-101.

[57] Guan G., Kaewpanha M., Hao X., Abudula A., *Catalytic steam reforming of biomass tar: prospects and challenges*, Renew. Sustain. Energy Rev., 58 (2016) 450–461.

[58] Valderrama-Riosa M.L., Martínez-González A., Lora E.E.S., Almazán del Olmo O.A., *Review Reduction of tar generated during biomass gasification: A review.*, Biomass and Bioenergy, 108 (2018)345-370.

[59] Corella J., Toledo J.M., Padilla R., *Olivine or dolomite as in-bed additive in biomass gasification with air in a fluidized bed: which is better?*, Energy Fuels, 18 (2004) 713–720.

[60] Ro D., Shafaghat H., Jang S.H., Lee H.W., Jung S.C., Jae J., Cha J.S., Park Y.K, *Production of an upgraded lignin-derived bio-oil using the clay catalysts of bentonite and olivine and the spent FCC in a bench-scale fixed bed pyrolyzer*, Environmental Research, 172 (2019) 658-664.

[61] Li S., Sanna A., Andresen J.M.,*Influence of temperature on pyrolysis of recycled organic matter from municipal solid waste using an activated olivine fluidized bed*, Fuel Processing Technology, 92 (2011) 1776-1782.

[62] Tuomi S., Kaisalo N., Simell P., Kurkela E., *Effect of pressure on tar decomposition activity of different bed materials in biomass gasification conditions*, Fuel, 158 (2015) 293–305.

[63] Wu C., Williams P. T., *Nickel-based catalysts for tar reduction in biomass gasification*, Biofuels, 2:4 (2011) 451-464.

[64] Arregi A., Lopez G., Amutio M., Barbarias I., Santamaria L., Bilbao J., Olazar M., *Kinetic study of the catalytic reforming of biomass pyrolysis volatiles over a commercial Ni/Al2O3 catalyst*, international journal of hydrogen energy, 43 (2018) 12023-12033.

[65] Valderrama Riosa M. L., Martínez González A., Lora E. E. S., Almazán del Olmo O. A., *Reduction of tar generated during biomass gasification: A review*, Biomass and Bioenergy, 108 (2018) 345–370.

[66] Sutton D., Kelleher B., Ross J. R. H., *Review of literature on catalysts for biomass gasification*, Fuel Processing Technology, 73 (2001) 155–173.

[67] Boroson M.L., Howard J.B., Longwell J.P., Peters W.A., *Heterogeneous cracking of wood pyrolysis tars over fresh wood char surfaces.*, Energy Fuels, 3 (1989) 735–40.

[68] A.V. Bridgwater, D. Meier, D. Radlein, *An overview of fast pyrolysis of biomass*, Org. Geochem., 30 (1999) 1479-1493.

[69] Abu El-Rub Z., Bramer E.A., Brem G., *Experimental comparison of biomass chars with other catalysts for tar reduction*, Fuel, 87 (2008) 2243–52.

[70] Gilbert P., Ryu C., Shari V., Swithenbank J., *Tar reduction in pyrolysis vapours from biomass over a hot char bed.*, Bioresour Technol, 100 (2009) 6045–51.

[71] Soria-Verdugo A., Morato-Godino A., Garcia-Gutierrez L.M., Garcia-Hernando N. *Pyrolysis of sewage sludge in a bubbling fluidized bed: determination of the reaction rate*, In: 12th International conference on fluidized bed technology (CFB 12), Krakow, Poland, 2017.

[72] Soria-Verdugo A., Morato-Godino A., Garcia-Gutierrez L.M., Garcia-Hernando N., *Pyrolysis of sewage sludge in a fixed and a bubbling fluidized bed - Estimation and experimental validation of the pyrolysis time*, Energy Conversion and Management, 144 (2017) 235-242.

[73] Weber K., Quicker P., *Properties of biochar*, Fuel, 217 (2018) 240–261.

[74] Reschmeier R., Roveda D., Müller D., Karl J., *Pyrolysis kinetics of wood pellets in fluidized beds*, Journal of Analytical and Applied Pyrolysis, 108 (2014) 117–129.

[75] Kalogiannis K.G., Stefanidis S.D., Karakoulia S.A., Triantafyllidis K.S., Yiannoulakis H., Mihailof C., Lappas A.A., *First Pilot Scale Study of Basic vs Acidic Catalysts in Biomass Pyrolysis: Deoxygenation Mechanisms and Catalyst Deactivation*, Applied Catalysis B: Environmental, 238 (2018) 346-357.

[76] Arregi A., Lopez G., Amutio M, Maite Artetxe M., Itsaso Barbarias I., Javier Bilbao J., Olazar M., *Role of operating conditions in the catalyst deactivation in the in-line steam reforming of volatiles from biomass fast pyrolysis*, Applied Energy, 237 (2019) 487-499.

[77] Yan Q., ToghianiH., Yu F., Cai Z., Zhang J., *Effects of pyrolysis conditions on yield of bio-chars from pine chips*, For. Prod. J., 61 (2011) 367-371.

[78] Fisher E.M., Dupont C., Darvell L.I., Commandré J.-M., Saddawi A., Jones J.M., Grateau M., Nocquet T., Salvador S., *Combustion and gasification characteristics of chars from raw and torrefied biomass*, Bioresource Technology, 119 (2012) 157–165.

[79] Konstantinos G. Kalogiannis, Stylianos D. Stefanidis, Angelos A. Lappas *Catalyst deactivation, ash accumulation and bio-oil deoxygenation during ex situ catalytic fast pyrolysis of biomass in a cascade thermal-catalytic reactor system*, Fuel Processing Technology, 186 (2019) 99–109.

[80] Di Blasi C. *Inuences of physical properties on biomass volatilization characteristics*, Fuel, 76 (1997) 957–64.

[81] Babu B.V., Chaurasia A.S., *Heat transfer and kinetics in the pyrolysis of shrinking biomass particle.*, Chem. Eng. Sci., 59 (2004) 1999–2012.

[82] Le T. A., Ly H. V., Kim J., *Catalytic Pyrolysis of Alga Saccharina japonica Using Co/-Al2O3 and Ni/-Al2O3 Catalyst*, Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 36:21 (2014) 2392-2400.

[83] Choi G.G., Oh S.J., Kim J.S., *Scrap tire pyrolysis using a new type two-stage pyrolyzer: Effects of dolomite and olivine on producing a low-sulfur pyrolysis oil*, Energy, 114 (2016) 457-464.

[84] Yang H., Yan R., Chen H., Lee D.H., Liang D.T., Zheng C., *Pyrolysis of palm oil wastes for enhanced production of hydrogen rich gases.* Fuel Process. Technol., 87 (2010) 935–942.

[85] Qian K., Kumar A., Zhang H., Bellmer D., Huhnke R. *Recent advances in utilization of biochar*, Renewable and Sustainable Energy Reviews, 42 (2015) 1055–1064.

[86] Rahman M., Liu R., Cai J., *Catalytic fast pyrolysis of biomass over zeolites for high quality bio-oil – A review* Md. Fuel Processing Technology, 180 (2018) 32–46.

[87] Hervy M., Olcese R., Bettahar M.M., Mallet M., Renard A., Maldonado L., Remy D., Mauviel G., Dufour A., *Evolution of dolomite composition and reactivity during biomass gasication*, Applied Catalysis, 572 (2018) 12023-12033.